

A HIGHER SCHOOL
INORGANIC CHEMISTRY



By E. J. HOLMYARD
M.A., M.SC., D.LITT., F.R.I.C.

A Junior Chemistry
Chemistry for Beginners
A Revision Course in Chemistry

* * *

A Text-book of Theoretical and Inorganic Chemistry

By F. A. PHILBRICK, M.A.
and

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Revised in collaboration with
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PREFACE TO THE ORIGINAL EDITION

HAVING prepared some hundreds of candidates in chemistry for the Higher Certificate examination of one examining body, and having examined several thousand candidates at the Higher Certificate examinations of other bodies, the author may perhaps claim, without offence to modesty, that he was not entirely unqualified to write a text-book suitable for Higher Certificate classes. The pages which follow are intended for students who have already reached the standard of the Ordinary Level of the General Certificate of Education in Chemistry, and work up to this stage has therefore been omitted, or only briefly recapitulated. It is assumed, for instance, that readers will be familiar with equations, equivalents, and the calculation of formulae from gravimetric composition, and with the simpler aspects of such phenomena as allotropy and thermal dissociation. It is also assumed that those who use the book will be simultaneously pursuing a course of appropriate practical work, and practical details have therefore not been included. On the other hand, the scheme and style of the book have been designed with certain important points in view. First, the allotment of space to individual topics is roughly in proportion to the frequency with which those topics appear in the examination papers. Exact proportionality is, of course, not possible; neither would it be desirable, (a) since some parts of the subject are more difficult than others and therefore require more deliberate treatment, and (b) since the cultural aspect of chemistry is seldom reflected in examinations, but must nevertheless receive due attention in a book which aspires to do something more than cram.

Second, those sections which deal with stock examination questions have been kept for the most part within such limits as may enable the candidate to reproduce them or their substance in half an hour. It is hoped that this feature will prove of real practical assistance, for examining experience shows that large numbers of candidates suffer from an inability to extract the gist of a subject and therefore write answers both diffuse and disproportioned.

Third, the book is provided with more than the usual number of cross-references, and with instructions for making comparative tables. The object is to encourage the student in his assimilation of chemical facts—a process more difficult now than formerly, owing to the shorter time commonly devoted to qualitative analysis. One of the most striking phenomena observable in Higher Certificate chemistry scripts is, indeed, the disparity between the candidates'

wide familiarity with chemical theories and their very limited first-hand acquaintance with chemical substances.

It may be well to add that the book contains sufficient general, theoretical, and physical chemistry, as well as descriptive chemistry, to form the main course of university scholarship candidates. No scholarship candidate, however, should confine himself to any one book; he should, rather, read widely, after having selected the book which is to be his principal guide.

It is my pleasure and privilege to acknowledge with gratitude the great help I have received from many individuals and firms in the preparation of this book. I am particularly indebted to my friends Professor W. Wardlaw, C.B.E., D.Sc., of Birkbeck College, Mr. N. F. Newbury, M.A., M.Sc., A.R.I.C., and Mr. A. J. Mee, M.A., B.Sc., who generously undertook to read the proofs, and who not only saved me from making many blunders but suggested numerous improvements. Mr. Newbury increased my obligation to him by spontaneously undertaking the preparation of the index, an amiability which evoked my warm appreciation. Two of my senior pupils at Clifton, T. I. Williams, Scholar of The Queen's College, Oxford, and F. J. M. Farley, Scholar of Clare College, Cambridge, also assisted in proof-reading, and showed that they could criticize my work with the same relentlessness that I employed upon theirs: a mutual pleasure. I must add that I alone bear the responsibility for any errors which may have escaped notice; but I trust they are few.

My thanks are also due to the following firms, who supplied me with information or illustrations: Imperial Chemical Industries Ltd., British Aluminium Company, British Commercial Gas Association, Borax Corporation, Imperial Smelting Corporation, B. Laporte, Texas Gulf Sulphur Company, International Agricultural Corporation, American Agricultural Chemical Corporation, E. G. Acheson Ltd., Carborundum Company, Chilean Nitrate Commission, and British Oxygen Company. For permission to reproduce the figures on p. 329 I have to thank Dr. H. Baines and the Editor of *Chemistry and Industry*.

Last, but certainly not least, I must express my thanks to the publishers, Messrs. J. M. Dent & Sons Ltd., from whom I have received every help and encouragement. I can only hope that readers will find the text of the book not unworthy of its attractive format.

E. J. H.

Note.—Examination and revision questions are not given in this book, since it was felt that the space could be more profitably employed.

PREFACE TO THE REVISED EDITION (1952)

FIFTEEN years have elapsed since this book was first published, and during that period it has been reprinted many times. In view of the continued demand, a new and revised version was clearly desirable, and the present edition has been entirely reset. With the collaboration of Dr. W. G. Palmer (Fellow of St. John's College, Cambridge) the text has been brought into accordance with modern knowledge and theory. The general scope has remained unchanged, and it is hoped that the book may continue to prove useful for senior forms in schools and for first-year undergraduates. The author wishes to thank the very numerous teachers and students who have written to him, whether in appreciation or to draw attention to inaccuracies which had escaped his attention in the previous edition. *Humanum est errare*, but the greatest care has been taken to check all the data and other facts in the pages which follow.

London.

E. J. H.

PREFACE TO THE REVISED EDITION (1963)

I REGRET to record the untimely death three years ago of the original author of *Higher School Inorganic Chemistry*. I was honoured to be invited by Dr. Holmyard to help in producing the revised (and re-titled) edition of 1952, and I am sure that he would have approved the changes I have made in 1963, as being 'in accordance with modern knowledge and theory,' and also with the contemporary aspirations of chemistry masters and their new and vigorous teaching projects.

Psychologists agree that 'unlearning' is even more difficult and arduous than learning, and this warning has been constantly before me in making textual innovations. In particular it has for too long been concealed from beginners that chemical kinetics cannot form a

sound basis of a quantitative and general law of chemical equilibrium. I have therefore ventured to build on to Chapter VII on 'Thermochemistry' a new chapter (XI) explaining, I hope in sufficiently simple and understandable form, the real basis of such a law. The concepts brought to light in this further chapter on chemical energy have thus been made available for many useful later applications, for example, in the new chapter (XVIII) on 'Electromotive Force.' Another aspect of 'unlearning' which can be exasperating to students concerns the literal symbols denoting physico-chemical quantities. There is now in existence an agreed system of symbols (published by the Chemical Society), and care has been taken to bring all those used in the book into agreement with that scheme.

The vital part played in both theoretical and practical chemistry in the first half of the nineteenth century by the early discoveries in the field of electrolysis seemed to warrant an earlier introduction of that subject, which now occupies Chapter IV. Today the sizes of atoms (and ions) play a part in chemical theory at least as important as their weights, and opportunities have been taken at various appropriate points in the text to emphasize this view, beginning in Chapter V, now under the expanded title 'Atomic Weight and Size,' with a simple account of the diffraction methods on which knowledge of size is mainly based. The mass-spectrograph, being now the main arbiter in fixing atomic weights, as well as a technique of great power in many other branches of chemistry, has also been given a place in Chapter V.

The central position that our rapidly developed understanding of the electronic and nuclear constitution of atoms should now occupy in expounding chemical science is no longer compatible with delaying the reader's acquaintance with this subject until the last chapter of Part I. An account in completely rewritten and expanded form now appears as Chapter IX, followed by a new chapter on 'Chemical Combination and Valency,' and immediately preceded by a largely rewritten chapter on 'The Classification of the Elements.'

The former chapter on 'Electrolytic Dissociation' has been divided into one (XVI) giving the general facts with an outline of modern theory, and another (XVII) devoted to the special field of 'Acids, Bases, and Salts.' The treatment in the new chapter is based on the modern definitions of an acid and a base.

In the detailed and factual inorganic chemistry of Part II fewer changes have been necessary. The transition metals (exemplified by chromium, manganese, iron, cobalt, and nickel) have been removed from the treatment by periodic groups rightly prevailing in previous chapters, and more stress is thereby laid upon inter-

comparison of these metals than upon their supposed group alliances. In a new and final chapter a brief account has been presented of some elements, for long known only as rarities in the laboratory, which have now emerged into prominence on the industrial scale (beryllium, titanium, germanium, molybdenum, tungsten).

I most gratefully acknowledge the generous and indispensable help received by being allowed to draw upon the experience and forward-looking suggestions of chemistry masters who are or have been my colleagues in school examining. In particular I here record my special gratitude to Mr. E. H. Coulson of Braintree, and to Mr. A. E. Ridler of Sheffield. To Messrs. Dent I am greatly indebted for the speed and meticulous care with which an exacting printing programme has been successfully carried through.

W. G. P.

F221

NOTE. In this book all *temperatures* are given on the Centigrade scale, except where otherwise stated. *Solubilities* given as a mere number are in grams of solute per 100 grams of solvent.

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PART I

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CHAPTER I

LANDMARKS IN THE HISTORY OF CHEMISTRY

As soon as man begins to think and to reason, the different objects which surround him on all sides naturally engage his attention. He cannot fail to be struck with their number, diversity, and beauty; and naturally feels a desire to be better acquainted with their properties and uses. If he reflect also, that he himself is altogether dependent upon these objects, not merely for his pleasures and comforts, but for his very existence, this desire must become irresistible. Hence that curiosity, that eager thirst for knowledge, which animates and distinguishes generous minds.

A System of Chemistry, by THOMAS THOMSON, 1802.

IN the year of grace 1802, chemistry was in the full flush of vigorous youth. New discoveries were being made in such rapid succession as to produce a feeling of exhilaration, almost of bewilderment; and the advance of chemical knowledge affected the general life so closely that—to use a line of WORDSWORTH'S—'*from touch of this new power, Nothing was safe.*' How vast the dominion of the 'new power' has subsequently become is plain even to the least observant; the 'generous mind,' therefore, will wish to be informed of the main course of events which led to so great an outburst of chemical activity.

The various branches of science have not arisen suddenly, each from a definite, individual point of origin. The biological maxim *omne vivum ex vivo*—all life arises from life—may be appropriately adopted to describe the development of chemistry, inasmuch as every stage of chemical progress is the natural outcome of an earlier one. To trace those stages as far into the past as the records make possible is a task that many scholars find superlatively attractive; but since the familiar features of modern chemistry are all comparatively recent, it will not here be necessary to take more than a passing glance at the earlier phases of chemical history. The curious reader may turn for more detailed information to the works mentioned at the end of this chapter, and to others of a similar character.

Chemistry. In A.D. 296 the EMPEROR DIOCLETIAN ordered the destruction of the Egyptian books on *chēmeia*, or chemistry, having a baseless fear that their possessors knew the art of converting cheaper metals into gold or silver and were thus in a position to finance an Egyptian rebellion against the Roman Empire. The word *chēmeia* is believed to come from the Egyptians' name for their

country, *qemi* or *qemt*, that is, the Black Land (a reference to the dark soil of the Nile Valley); so that chemistry originally meant the Egyptian Art, or the Art of the Black Land.

Ancient Chemistry. In ancient times, among the Egyptians, Assyrians, Chinese, Hindus, Greeks, and Romans, there was no such chemical science as is known to the modern world. The chemistry of those days was represented by metallurgy, pottery, glass-making, pharmacy, brewing, dyeing, and similar arts and crafts; and, while the number of chemical facts familiar to the workers must have been very great, no serious attempt was made to arrange or investigate them as the units of a distinct branch of knowledge.



FIG. 1. ARISTOTLE

Chemical Theory. The beginnings of chemical theory, as contrasted with chemical practice, are to be found in the speculations of the Greek philosophers — PLATO, ARISTOTLE, EMPEDOCLES, DEMOCRITUS, and their fellows—concerning the nature of the world as a whole. Among these speculations was one which supposed all matter to be composed of four 'elements,' *fire, air, earth, and water*, the difference between one kind of matter and another lying in the different

relative proportions in which these 'elements' were present in them. If this supposition were true, it should be possible to convert any one substance into any other by a suitable adjustment of the four 'elements,' and a theoretical justification was thus provided for the operation whose alleged success had disturbed Diocletian.

Alchemy. For some 1,800 years (300 B.C.—A.D. 1500), the transmutation (i.e. conversion) of the base or inexpensive metals into gold and silver was, indeed, the principal object of chemists. Pursued first in Alexandria and other cities of Egypt, this fantastic quest was taken up with redoubled energy by the Arabs in the eighth and succeeding centuries; and their enthusiasm quickly infected Europe with a passion for *al-chemy*.* CHAUCER (about 1340—

* *Al* is the Arabic definite article.

1400), in his *Canterbury Tales*, bitterly attacks the numerous fraudulent alchemists, who swindled credulous people by pretending to have discovered the elixir or philosophers' stone, which could convert unlimited quantities of lead or mercury into the purest gold.

Iatrochemistry. A new and better aim was given to chemistry by the eccentric, almost Rabelaisian, Swiss physician PARACELSUS (1493-1541), who, while by no means a disbeliever in the claims of the alchemists, urged them to devote their energies rather to the production of improved drugs for use in medicine. Paracelsus gained a wide following, and the period from his lifetime to the



FIG. 2. PARACELSUS



FIG. 3. THE HON. ROBERT BOYLE

closing years of the seventeenth century is consequently known as the age of *iatrochemistry*, i.e. medical chemistry.

The Birth of Modern Chemistry. The alchemists and iatrochemists, during their unwearied exertions in smoky laboratories, had gathered together a vast quantity of information—much vague, but some precise—concerning the properties of metals, minerals, and other substances, and had discovered such important reagents as sulphuric, nitric, and hydrochloric acids, silver nitrate, mercuric chloride, and potassium nitrate. The later iatrochemists had also done much to free chemistry from the superstitions and magical practices with which the alchemists had encumbered it. The time had therefore come when it was possible for a true chemical science to arise—a science to be studied for its own sake and not as a mere subordinate to medicine.

The man who first perceived this possibility, and strove with some measure of success to achieve it, was the HON. ROBERT BOYLE

Black's work attracted a good deal of attention, and chemists began to feel that changes in weight during chemical action were of fundamental importance. In consequence, the increase in weight of metals upon combustion came to be regarded as a grave objection to the phlogiston theory.

The second development was a rapid extension in the study of gases. Carbon dioxide, as we have seen, was studied by Black.



National Portrait Gallery

FIG. 7. J. PRIESTLEY

Hydrogen was discovered in 1766 by CAVENDISH, while PRIESTLEY, in a brilliant period round 1770, discovered the gases we now call oxygen, sulphur dioxide, hydrogen chloride, and nitrous oxide. Chlorine was discovered about the same time by SCHEELE, and nitrogen by D. RUTHERFORD. Priestley obtained oxygen by heating 'calx of mercury' (HgO), which he regarded as mercury that had lost its phlogiston; the gas he regarded as dephlogisticated air, i.e. air from which the phlogiston normally present in it had been removed. He was unable, however, to account for its formation, but did not doubt the adequacy of the phlogiston theory.

Lavoisier. In France, the young chemist LAVOISIER (1743-94) had already proved that air is a mixture of at least two gases. Upon heating a known weight of tin in a sealed flask filled with air, he found (a) that the total weight of the apparatus remained unchanged, (b) that about one-fifth, but no more, of the air in the flask disappeared, and (c) that the residual tin and tin ash (calx) weighed more than the original tin by an amount approximately equal to the weight of the air that had vanished. He concluded that one-fifth of the air was 'active' and the other four-fifths 'inactive.'

On the occasion of a visit to Lavoisier in Paris, Priestley mentioned his discovery of 'dephlogisticated air' and described its remarkable power of supporting combustion. Lavoisier realized that Priestley had accidentally stumbled upon a method of obtaining 'active' air in a state of purity. Modifying Priestley's experiment, Lavoisier heated 4 oz. of mercury for several days in an enclosed volume of 50 cu. in. of air, and found that the mercury became covered with a red powdery scale. At the same time, the volume of the air diminished to 42 cu. in., subsequently remaining

unchanged. The residual air would not support combustion or life; to it he gave the name *azote*.* The red powder weighed 45 grains. When heated, it yielded 8 cu. in. of 'active' air and 41.5 grains of mercury. On mixing the 'active' air with the 42 cu. in. of azote, 50 cu. in. of a gas exactly resembling the original air was obtained, without any sign of a chemical action.



Dr. D. McKee

FIG. 8. A. L. LAVOISIER AND HIS WIFE

On the basis of this and many similar experiments, Lavoisier concluded that phlogiston had no existence, and that combustion consisted in a union of the burning substance with the active portion of the air. Such an explanation not only elucidated the facts already 'explained' by the phlogiston theory, but offered a

* The name *nitrogen* was suggested by CHAPTAL in 1790. In France, the gas is still called *azote*.

convincing reason for the increase in weight that accompanies combustion.

After some hesitation, chemists—with the notable exception of Priestley—acclaimed Lavoisier's theory of combustion, 'look'd at each other with a wild surmise,' and enthusiastically undertook the revision and extension of chemistry in the light of the new knowledge. Lavoisier himself had but few years to live, falling a victim to the guillotine during the Terror; but he had time to discover that 'active' air is a very frequent, if not invariable, constituent of acids, and for this reason he decided to name it *oxygen* (Greek, acid-producer).

A second great service to chemistry performed by Lavoisier, in company with certain other French chemists, was the establishment

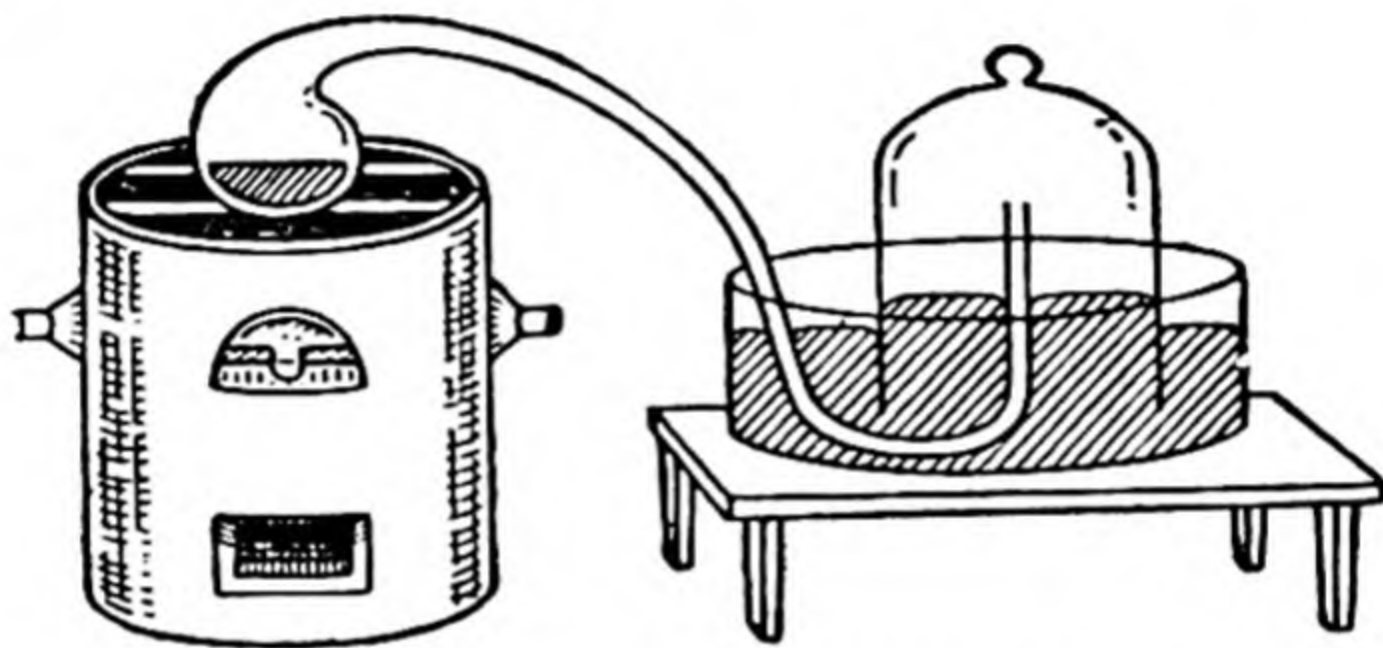


FIG. 9. LAVOISIER'S EXPERIMENT

of the modern system of chemical nomenclature. In the report which they drew up in 1787, we meet for the first time with such familiar terms as sulphate, sulphite, sulphide, nitrate, and carbonate, instead of the old 'kitchen' names (e.g. liver of sulphur, butter of antimony, sugar of lead, milk of lime) which were difficult to remember and threw no light upon the constitution of the substances concerned.

The Early Nineteenth Century. Only a decade or so after Lavoisier's death, the next great advance in chemistry was made—this time by the Englishman JOHN DALTON (1766–1844). Dalton's fame rests upon his establishment of the *atomic theory of matter*, and since this forms the subject of the next chapter it may here be left with a mere passing mention.

The idea of atoms and molecules soon became an integral part of the chemist's intellectual equipment, and the work of GAY-LUSSAC (1778–1850), AVOGADRO (1776–1856), DULONG (1785–1838) and PETIT (1791–1820), and others enabled many atomic and molecular

weights to be determined. BERZELIUS (1779-1848) introduced the present notation of symbols, formulae, and equations as early as 1811-14, but this aid to precision of thought and expression took several years to become popular.

Meanwhile, many new elements had been discovered and their properties and compounds studied. In

1800-1 VOLTA (1745-1827) had invented the first electric battery, a device which in the hands of SIR HUMPHRY DAVY (1778-1829) led

within a few years to the isolation of sodium, potassium, calcium, strontium, barium, and magnesium.

Between 1801 and 1810 niobium, tantalum, cerium, palladium, rhodium, osmium, iridium, and boron were discovered.

Iodine followed in 1812, lithium and cadmium in 1817, selenium in 1818, thorium in 1828. Chemical industry was assuming large dimensions, and presented chemists with problems the solution of which often led to further advances in the theory and practice of the subject.

Berzelius's Electrochemical Theory. In 1806, Davy suggested that chemical combination is an electrical phenomenon. Some years later (1811-19), Berzelius elaborated this suggestion in the form of his 'electrochemical' or 'dualistic' theory. He assumed all atoms to be electrically

charged and to show a polarity, i.e. to possess positive and negative poles. The two poles are not equal in strength; in



Royal Institute of Chemistry

FIG. 10. J. J. BERZELIUS



The Clarendon Press, Oxford

FIG. 11. SIR HUMPHRY DAVY

some cases the positive pole is stronger than the negative, and in others the negative predominates. Because of this excess of polarity, elements are either electronegative or electropositive, appearing at the anode or cathode respectively in electrolysis. The degree of chemical activity of a substance depends upon its intensity of polarization, which itself varies with the temperature. Chemical combination consists in the (more or less complete) neutralization of electricity between oppositely charged poles, and since each atom has both a positive pole and a negative pole it is not impossible for two electronegative elements to combine with one another, or two electropositive ones, though in general, of course, combination normally occurs between elements of opposite electrical character.

When an electropositive element combines with an electronegative element, the molecules of the compound so formed may still show a predominating residual polarity. Thus when copper (+) combines with oxygen (—), the copper oxide molecules are still slightly electropositive, while sulphur trioxide—in which the positive pole of the sulphur neutralizes part of the negative electricity in the oxygen—is electronegative. Copper oxide can therefore combine with sulphur trioxide to form copper sulphate; but even this compound shows slight polarity and is able to combine with other substances (e.g. water) to form more complex substances, and so on.

Such were the views of Berzelius upon chemical combination. They were generally accepted, and led quickly to great progress in the investigation of molecular structure. Finally, however, facts were discovered that caused them to be abandoned in their original form; yet Berzelius's main hypothesis, viz. that there is an intimate connection between chemical and electrical forces, has been revived in recent years and its truth is now universally assumed.

The Approach to the Present Day. By the middle of the nineteenth century, chemistry had begun to exhibit many of the features familiar to us to-day. Several of the chief further developments are considered in this book in the appropriate chapters. Those who are interested in chemical history may refer to the books mentioned below.

BOOKS FOR FURTHER READING

- J. READ: *Prelude to Chemistry*. (G. Bell & Sons Ltd.)
J. R. PARTINGTON: *A Short History of Chemistry*. (Macmillan & Co. Ltd.)
E. J. HOLMYARD: *Makers of Chemistry*. (Oxford University Press.)
T. M. LOWRY: *Historical Introduction to Chemistry*. (Macmillan & Co. Ltd.)
H. M. LEICESTER: *Historical Background of Chemistry*. (J. Wiley; Chapman & Hall.)

CHAPTER II

THE SIMPLE ATOMIC THEORY

The Structure of Matter. For everyday purposes, and for elementary scientific purposes, matter may still be conveniently described in the old way, namely as 'that which has weight and occupies space.' The idol made of wood or stone is material, but the emotion it arouses in the mind of its heathen worshipper is as immaterial as the light of the tropic sun that illuminates it.

To the philosophers of classical antiquity the problem of the structure of matter presented itself as a mere choice of simple alternatives: matter is either (a) *continuous* or (b) *discrete*, that is, it is capable either of infinite subdivision, or of subdivision only up to a certain point. In the latter event, the particles finally reached must, by hypothesis, be incapable of further division and can therefore be described as *atoms* (Greek, *indivisible*). Both of these alternative views found skilful supporters. LEUCIPPUS (sixth century B.C.), DEMOCRITUS (about 460–357 B.C.), and, later, LUCRETIUS (about 98–55 B.C.) argued brilliantly for the atomic structure of matter, while ARISTOTLE (384–322 B.C.) was its chief opponent. Neither side, however, was able to bring what we should now describe as experimental evidence in support of its contentions, and the controversy became a mere verbal debate. The importance of experiment, and especially of controlled experiment, was not yet realized; neither were there yet the means of conducting appropriate experiment. In the event, the authority of Aristotle overbore his opponents, and the atomic theory retired into obscurity with a parting thrust from GALEN (second century A.D.).

Revival of the Atomic Theory. The view that matter is composed of minute indivisible atoms did not, however, vanish completely from human thought, and the poet BEN JONSON spoke in 1618 of an Englishman who declared himself in agreement with Democritus. Later on in the seventeenth century, the atomic theory became widely familiar through the writings of GASSENDI (1592–1655) and DESCARTES (1596–1650), though these philosophers, like their Greek predecessors, made little attempt to reinforce their arguments by appeal to observational facts and experiment. A much higher dignity attached to the theory when it was adopted by

Relations of Dalton's Theory to Experiment. Dalton's form of the atomic theory represented an immense advance on the older speculations inasmuch *as it could be, and was, tested by experiment.*

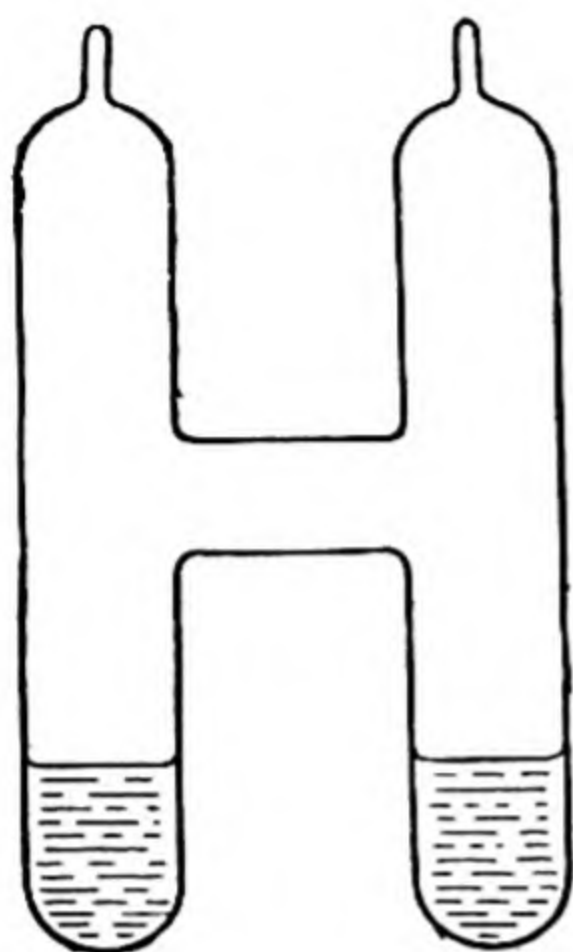


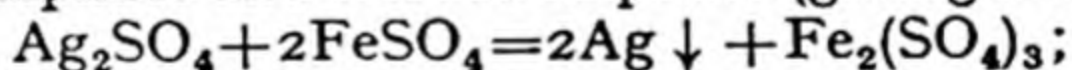
FIG. 14.
LANDOLT'S TUBE

In the first place, if matter is composed of indestructible and uncreatable atoms, then it must itself be indestructible and uncreatable. This fact had already been adumbrated by the quantitative researches of BLACK and LAVOISIER, and may be expressed in the form of the *Law of the Conservation of Matter: matter can neither be created nor destroyed.* Over a century of subsequent work has abundantly proved the general truth of this law, though modern investigation of radioactivity and electrical phenomena has shown that, under some conditions, matter may be converted into energy. In ordinary chemical reactions, the law holds with very great accuracy, as was demonstrated by LANDOLT (1831-1901).

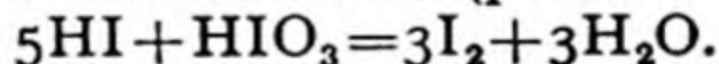
In the limbs of a Jena-glass H-tube or U-tube (Fig. 14), Landolt sealed solutions of substances which, when mixed, would react with little heat change (any errors

likely to be made by wide fluctuations of temperature thus being avoided). Among the substances employed were:

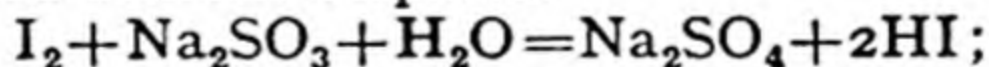
- (i) Silver sulphate and ferrous sulphate (giving silver on mixing):



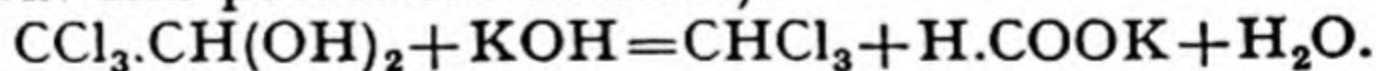
- (ii) Hydriodic acid and iodic acid (producing iodine):



- (iii) Iodine and sodium sulphite:



- (iv) Chloral hydrate and potassium hydroxide (yielding chloroform and potassium formate):



On bringing about these reactions by allowing the reactants to mix, no measurable final change in total weight could be detected in any instance. Hence, as Landolt was working to an accuracy of one part in ten million (10,000,000), any change in weight that might have taken place must have been smaller than this. Improved methods subsequently employed by J. J. MANLEY (1912) have demonstrated that any possible change in weight must be less than one part in a hundred million (100,000,000) in the reactions he studied.

RELATIONS OF DALTON'S THEORY TO EXPERIMENT 17

At the present day, it is known (as stated above) that matter is capable of being transformed into energy; but the amount of energy derivable from even a minute weight of matter is so great that, in all ordinary chemical reactions—even the most vigorous—the fraction of matter so converted would be quite undetectable. According to Einstein's equation, the absolute energy of a mass m is $E=mc^2$, where c is the velocity of light. On this basis 1 gm. mass is equivalent to 8.99×10^{20} ergs.

A second law of chemistry for which Dalton's theory provides a simple explanation is the *Law of Constant Composition*, viz. that *all specimens of any particular compound possess the same composition by weight*. If Dalton's theory is correct, this law follows from the third assumption (p. 15): for all the molecules of the compound are assumed to be exactly similar, and therefore must possess a uniform composition. Two specimens of carbon monoxide, prepared in distinct ways (p. 400), each consist of molecules of carbon monoxide, all of which are alike and consist of one atom of carbon and one of oxygen. But, by the theory, all atoms of carbon exactly resemble one another, and so do all the atoms of oxygen. Hence the composition by weight of all carbon monoxide molecules must be the same, and so must that of all masses composed of these molecules.

LAVOISIER (1743–94) appears to have assumed the truth of the law of constant composition; and his fellow countryman, PROUST (1755–1826), relying on his own analyses of some solid substances, so strenuously supported it that he was drawn into an extended controversy with BERTHOLLET (1784–1822), who denied the universal applicability of the law. The exactitude of analytical methods at this period was probably insufficient to settle such a dispute. In the work of the Belgian chemist STAS (on the determination of atomic weights, published 1860–5) a much higher standard of accuracy was reached.

Stas took several different samples of silver purified in various ways, dissolved them separately in nitric acid, and determined the weights of sodium chloride required to convert (by precipitation) a fixed weight of the silver into silver chloride. Letting the weight of salt used for the first specimen of silver be 100.000, he found the weights for the others to be:

Specimen of Silver	Weight of Salt required
[1]	[100.000]
2	99.998
3	99.999
4	99.997
5	99.994
6	99.995
7	99.999
8	99.997

Up to the limit of accuracy attained in this research the law holds for both sodium and silver chlorides. Subsequent work by many chemists, especially in the field of atomic weight determination (Chapter V), proved the validity of the law to a similar or higher exactitude for a wide range of chemical compounds.

Recent developments have shown, however, that in respect to certain solid compounds of the metals Berthollet's scepticism was not wholly unjustified. For example, a small but definite variability of composition has been detected in some metallic oxides, such as ferrous oxide (FeO) and cuprous oxide (Cu_2O), wherein there is always a slight deficiency of metal up to a maximum of about 1 per cent. The formulae would therefore be more accurately expressed as $\text{Fe}_{(1-d)}\text{O}$ and $\text{Cu}_{(2-d)}\text{O}$. In iron nitride, Fe_4N ($\text{N}=5.90$ per cent), a homogeneous grey solid yielding all its nitrogen as ammonium chloride, NH_4Cl , on dissolving in dilute hydrochloric acid, the percentage of nitrogen varies from 5.7 to 6.1 per cent. In ferrous sulphide, familiar in Kipp's generator of hydrogen sulphide, the percentage of sulphur varies from 36.5 (FeS) to 40.7 ($\text{Fe}_{0.83}\text{S}$), depending on the proportions of metal and sulphur fused together in its preparation. Deviations from the law of constant proportions are thus illustrated by compounds of iron and copper, but these metals are not exceptional in this respect. Solid compounds proved to be variable in composition are often referred to, not inappropriately, as *berthollides*.

The Law of Multiple Proportions. The law of multiple proportions states that *if two elements (or radicals) combine together to form more than one compound, then the weights of one element (or radical) which combine with a fixed weight of the other element (or radical) are in a simple multiple ratio to one another*. This law is particularly interesting since Dalton first deduced it from his atomic theory, and afterwards demonstrated its truth by actual experiment. It is a direct corollary of point 5 (p. 15), viz. that the molecules of compounds consist of *small* numbers of atoms; for if, in two different compounds of the elements X and Y, the numbers of atoms of X and Y in the two different molecules are both small, then the number of atoms of Y which combine with, say, one atom of X in the first compound, and the number of atoms of Y which similarly combine with one atom of X in the second compound, must also both be small. Hence their ratio must be a simple one; and since all the molecules of each compound have exactly the same composition, this simplicity must extend to the ratio of the weights of Y which combine with *any* fixed weight of X, not merely to one 'atom-weight.'

Suppose, for example, that the elements X and Y combine to form the compounds XY and X_2Y_3 . Then, taking one atom as

the fixed weight of X, the ratio of the weights of Y which combine with the fixed weight of X in the two different compounds is $\frac{Y}{\frac{3}{2}Y} = 2 : 3$. Now suppose we take as the fixed weight of X a conveniently weighable quantity, such as 1.00 gm. This will contain an indeterminate number, say n , atoms of X, and in the first compound will be combined with n atoms of Y. Similarly, in the second compound, 1 gm. or n atoms of X will be combined with $n \times \frac{3}{2}$ atoms of Y. But since all the atoms of Y are alike in weight, the ratio of the weights of Y which combine with the fixed weight (1 gm. or n atoms) of X will be $\frac{n}{n \times \frac{3}{2}} = 2 : 3$, as before.

Example: On analysis, three oxides of manganese were found to contain respectively 63.2, 69.6, and 77.5 per cent of manganese. Taking 1.00 gm. of manganese as the fixed weight of one element, the weights of oxygen combining with this weight of manganese in the three oxides are $\frac{100-63.2}{63.2}$, $\frac{100-69.6}{69.6}$, and $\frac{100-77.5}{77.5}$ gm. respectively; that is, 0.582, 0.437, and 0.290. These numbers are very closely in the simple ratio 4 : 3 : 2; hence in this case the law of multiple proportions is true, within the limits of the experimental data.

The law may also be applied to the combination of radicals, such as $>SO_4$, $>CO_3$, NH_4- , and of water of crystallization and other complete molecules.

Example: Anhydrous sodium carbonate will combine with water to form two different hydrates, containing respectively 62.9 and 14.5 per cent of water of crystallization. Are these figures in agreement with the law of multiple proportions?

Choosing 1 gm. of anhydrous sodium carbonate as the fixed weight of one substance, the relevant weights of water will be $\frac{62.9}{100-62.9}$ and $\frac{14.5}{100-14.5}$, i.e. 1.7 and 0.17. The ratio is therefore 10 : 1, and the law is obeyed.

It must be admitted that, while most inorganic substances follow the law of multiple proportions (since the formulae expressing their composition contain few symbols), organic (carbon) compounds with large molecules do not come within its scope. In the hydrocarbons $C_{60}H_{122}$ and $C_{60}H_{120}$, for instance, the ratio of the weights of hydrogen

which combine with a fixed weight of carbon is 122 : 120 or 61 : 60, which can hardly be regarded as simple. 'Simple' is, to be sure, a vague term, but in this connection it is usually confined to a ratio that can be expressed by single figures (e.g. 9 : 8 but not 11 : 10 or 10 : 9). Dalton was fortunate in the fact that, of the many organic substances already known in his time, he happened to select compounds with such small molecules as methane (CH_4) and ethylene (C_2H_4) for his experiments on multiple proportions. Among the inorganic compounds he analysed were the two oxides of carbon and the three common oxides of nitrogen (N_2O , NO , NO_2).

Note that, in working out a problem on the law of multiple proportions, *any* weight may be selected as the fixed weight, and this weight may be taken of *either* element (radical, or molecule). The choice is most conveniently settled by considering what fixed weight will give the least trouble in calculation.

The complete establishment of the law was effected by the Swedish chemist J. J. BERZELIUS (1779–1848), who, in the years 1808–12, analysed with great accuracy a vast number of salts and other compounds. His analytical figures were such that he wrote to Dalton: 'You are right in this, that the theory of multiple proportions is a mystery without the atomic hypothesis: and as far as I have been able to see, all the results gained hitherto contribute to justify this hypothesis.'

The Law of Reciprocal Proportions (discovered by RICHTER, 1762–1807, and Berzelius) may also be deduced from Dalton's theory. It states that *if the elements A and B combine together in the ratio by weight $x : y$, and A and C combine together in the ratio $x : z$, then if B and C combine together (or combine, separately, with another element), they do so in the ratio by weight $y : z$ or in some simple multiple or submultiple of this ratio.*

As a formal statement, this law sounds much more complex than it really is. It will be understood best by taking a definite example: Silver (A) combines with oxygen (B) and also, separately, with chlorine (C). The ratio by weight $\frac{\text{oxygen}}{\text{silver}}$ is 0.074, and the ratio $\frac{\text{chlorine}}{\text{silver}}$ is 0.329. The law states that if oxygen and chlorine combine together—which they do—the ratio by weight $\frac{\text{oxygen}}{\text{chlorine}}$ should be a simple multiple or submultiple of the ratio $\frac{0.074}{0.329}$, i.e. of 0.225. Experiment shows that in chlorine monoxide the ratio $\frac{\text{oxygen}}{\text{chlorine}}$ is 0.225, and in chlorine dioxide 0.900, i.e. 0.225×4 . Hence

in both these oxides of chlorine the ratio $\frac{\text{oxygen}}{\text{chlorine}}$ is in accordance with the predicted result.

The law of reciprocal proportions follows from Dalton's assumption that the molecules of compounds consist of *small* numbers of atoms; it fails, like the law of multiple proportions, in the case of molecules consisting of large numbers of atoms.

Symbols and Formulae. DALTON represented the atoms of the various elements by circles, with lines, dots, or letters within them, and the 'compound atoms' or molecules of substances by appropriate groupings of these elementary symbols. \odot , for example, stood for one atom of copper, \circ for one atom of oxygen, \bullet for one atom of carbon, and $\circ\bullet\circ$ for one molecule or ultimate particle of carbon dioxide. This system was extremely cumbersome, and many of the symbols were difficult to remember; but fortunately, in 1814 or perhaps a little earlier, BERZELIUS suggested a much more convenient method, which is, in essentials, the one that we now employ. Since this will be familiar to readers of the present book, it is unnecessary to give further details here.

Relative Weights of Atoms and 'Compound Atoms.' Earlier in this chapter we saw that, according to Dalton, it is both important and possible to determine the relative weights of atoms and of the 'compound atoms' or molecules of compounds. How Dalton himself set about this fundamental problem is well worth considering, as an example of scientific method. It was, at that time, a comparatively easy matter to conduct the quantitative analysis of compounds not too complex in nature. Dalton found, for example, that in water the proportion by weight of oxygen to hydrogen is roughly 8 : 1. If this proportion is true for water in bulk, it must be equally true for the smallest possible particle of water, viz. the molecule. Now, supposing that the water molecule consists of n atoms of oxygen and m atoms of hydrogen, the weight of the oxygen atom relatively to that of the hydrogen atom will be $\frac{8}{n} : \frac{1}{m}$;

hence if n and m were known the weight of the oxygen atom in terms of the weight of the hydrogen atom could be calculated.

It was here that the difficulty lay, for there appeared to be no way in which the number of atoms in a molecule could be discovered. To avoid this difficulty, Dalton took a bold step. He decided that, if only one compound of a given pair of elements was known, he would assume that the molecule of that compound consisted of *one* atom of each element; that if two compounds consisting of the same two elements (say A and B) were known, the molecule of one should be regarded as consisting of *two* atoms of A

and *one* of B (or *two* of B and *one* of A); and so on. He felt that, by making this assumption, provisional relative weights could be obtained, and that with the accumulation of experimental facts any errors made would gradually be put right.

At that time, water was the only known compound of hydrogen and oxygen; hence Dalton assumed that the molecule of water consisted of one atom of each of these elements. Then since the proportion by weight of oxygen to hydrogen in water is 8 : 1, this must also be the ratio of the weights of the oxygen and hydrogen atoms. Dalton therefore adopted 8 as the 'atomic weight' of oxygen. In the same way, assuming the molecule of ammonia to consist of one atom of nitrogen and one of hydrogen, he obtained a value of 4.7 for the atomic weight of nitrogen.

Both of these values were, as we now know, erroneous, because the assumptions made about the structures of the water and ammonia molecules were incorrect. With carbon monoxide and dioxide, however, Dalton was more fortunate, since he guessed carbon monoxide to be CO and the dioxide CO₂; here, therefore, he obtained the true relation between the weights of the atoms of carbon and oxygen—though by taking the atomic weight of oxygen (in terms of hydrogen) to be 8, he gave carbon an atomic weight of 6.

Applying the method to compounds, he published values for the relative weights of their ultimate particles or molecules in terms of the weight of the atom of hydrogen. These values could not, of course, be regarded as final, because the fundamental difficulty—namely lack of knowledge of the number of atoms in a molecule—still remained unsolved. How this problem was at length successfully tackled we shall see in the next chapter.

CHAPTER III

MOLECULAR WEIGHTS

He that weighs the winds must have steady hands.

LYLY

The Gas Laws. Before proceeding with the atomic and molecular theory, it is necessary to consider some of the properties of gases, for it was directly from work upon gases that the next advance was made. The reader will already be acquainted with the simple gas laws, but for convenience they are given in a summary form below:

Boyle's Law states that *the volume occupied by a given mass of gas varies inversely as the pressure upon it, if the temperature is constant.* If, for instance, a gas occupies a volume V at a pressure P , and a volume V' at a pressure P' , it will be found that $PV = P'V'$; in other words, $PV = \text{a constant}$ (if the temperature is constant).

Example (i): A quantity of oxygen occupies a volume of 115 c.c. at 700 mm. pressure. What volume will the gas occupy at 280 mm. pressure, if the temperature remains unchanged?

$$\begin{aligned}PV &= P'V' \\ \therefore 115 \times 700 &= 280 \times x \\ \therefore x &= \underline{287.5 \text{ c.c.}}\end{aligned}$$

Note that the pressure here is expressed as a *length*; the reference is to the height of a vertical column of mercury that the pressure could support. A pressure of 760 mm. of mercury is known as *normal* or *standard* pressure. High pressures may be conveniently expressed in 'atmospheres,' where 1 atmosphere = 760 mm. of mercury.

Example (ii): Some nitrogen, occupying 246 c.c., is at a pressure of one atmosphere. If it is introduced into an evacuated globe of 2 litres capacity, what will be the pressure in the globe? (T constant.)

$$\begin{aligned}PV &= P'V' \\ \therefore 246 \times 760 &= x \times 2000 \\ \therefore x &= 93.5 \text{ mm.}\end{aligned}$$

Charles's Law was discovered by the Frenchman CHARLES * about

* For an amusing account of Charles and his celebrated ascent in the first balloon to be filled with hydrogen, see G. Lenotre, *Paris et ses Fantômes*, p. 104 (Paris, Grasset, 1933).

1787, but was first published by GAY-LUSSAC (1778–1850) in 1802. It states that, *provided the pressure remains constant, the volume of a given mass of gas increases by $\frac{1}{273}$ of its volume at 0° C. for every rise in temperature of one Centigrade degree.* Put in a more useful way, this means that, *at constant pressure, the volume of a given mass of gas varies directly as the ABSOLUTE temperature (i.e. Centigrade temperature + 273°).* If, for example, a gas occupies V c.c. at an absolute temperature of T° , and V' c.c. at T'° , then $VT' = V'T$.

Example (i): A quantity of hydrogen occupies 125 c.c. at 17° C. What volume would the gas occupy at 100° C., the pressure remaining constant?

$$\begin{aligned} VT' &= V'T \\ 17^\circ \text{ C.} &= 290^\circ \text{ Abs.}; 100^\circ \text{ C.} = 373^\circ \text{ Abs.} \\ \therefore 125 \times 373 &= x \times 290 \\ \therefore x &= \underline{161 \text{ c.c.}} \end{aligned}$$

Example (ii): A quantity of helium occupies 142 c.c. at 27° C. To what Centigrade temperature must the gas be heated in order that it may occupy 1,000 c.c. at the same pressure?

$$\begin{aligned} VT' &= V'T \\ 27^\circ \text{ C.} &= 300^\circ \text{ Abs.} \\ \therefore 142 \times x &= 1,000 \times 300 \\ \therefore x &= 2113^\circ \text{ Absolute} \\ &= \underline{1840^\circ \text{ C.}} \end{aligned}$$

Normal or Standard Temperature is taken as 0° C. (i.e. 273° Absolute). N.T.P. or S.T.P. is used as a contraction for Normal (or Standard) Temperature and Pressure, viz. 0° C. 760 mm. It is worth remembering that in correcting volumes of gases *to* N.T.P., the 273 comes at the top and the 760 below. In correcting *from* N.T.P. the reverse is true.

From Boyle's Law and Charles's Law it follows that, provided the volume is kept constant, the pressure exerted by a given mass of gas is directly proportional to the Absolute temperature:

$$PT' = P'T.$$

All three laws may be expressed in the formula:

$$\frac{PV}{T} = \text{a constant,}$$

where the constant is proportional to the mass of gas, and different constants are required for equal masses of different gases. See also p. 32.

In this simple form, the equation is accurately true only for a hypothetical 'perfect' gas. No known gas is by any means 'perfect,' but the deviations in behaviour will be discussed later (p. 61).

NOTE. If a gas is allowed to remain in contact with sufficient water, it will become saturated with water-vapour, and the total pressure becomes $P_{\text{gas}} + P_{\text{water-vapour}}$. In this case the effective pressure of the dry gas itself is the external pressure on the moist gas minus the pressure of aqueous vapour (water-vapour) at the temperature concerned. Thus, suppose some hydrogen is saturated with water-vapour at 14°C. , and that the moist gas is at a pressure of 755 mm. Then the effective pressure of the hydrogen is 755 mm. minus the pressure of aqueous vapour at 14°C. This can be found from the tables—it is 12 mm.; therefore the effective pressure of the hydrogen is $755 - 12$, i.e. 743 mm. (See Dalton's Law of Partial Pressure, below.)

Example: Some oxygen, collected over water, occupied 35 c.c. at 6°C. 765 mm. Find its volume *dry* at N.T.P.

Pressure of aqueous vapour at $6^{\circ}\text{C.} = 7\text{ mm.}$

$$\therefore \text{true pressure on the oxygen} = 765 - 7 \\ = 758\text{ mm.}$$

$$\therefore \text{volume at N.T.P.} = \frac{35 \times 758 \times 273}{760 \times 279} \\ = \underline{\underline{34.2\text{ c.c.}}}$$

Dalton's Law of Partial Pressure. The total pressure of a mixture of gases is the sum of the partial pressures of the gases composing it; that is, it is the sum of the pressures which each gas would exert if it were confined alone in the volume occupied by the mixture.

Combination of Gases by Volume. Some seven years after his publication of Charles's Law, Gay-Lussac announced the discovery of a further important law concerning gases. This law, known after its discoverer, or alternatively as the *Law of Gaseous Combining Volumes*, is that *when gases react, the volumes in which they do so are in a simple ratio to one another, and to the volume of the product or products if gaseous.* Gay-Lussac found, for example, that 100 volumes of oxygen unite with 200 volumes of hydrogen (ratio 1 : 2); that 100 volumes of hydrogen chloride combine with exactly 100 volumes of ammonia (ratio 1 : 1); and that sulphur trioxide is formed by the combination of sulphur dioxide with *half* its own volume of oxygen.

Moreover, if the combination of oxygen and hydrogen is brought

about at a temperature greater than 100°C. , so that the water produced is retained in the gaseous form, then

1 volume of oxygen reacts with 2 volumes of hydrogen to give 2 volumes of steam.

Similarly 2 volumes of ammonia, on decomposition, will yield 1 volume of nitrogen and 3 volumes of hydrogen—assuming in this, as in the previous examples, that all the measurements are taken at the same temperature and pressure.

Avogadro's Principle. To explain Gay-Lussac's Law—as well as to afford a partial explanation of Boyle's Law, Charles's Law, and the general similarity of physical behaviour shown by gases—a hypothesis was suggested in 1811 by AMADEO AVOGADRO (1776–1856), Professor of Physics at the University of Turin (Italy). Avogadro had come to the conclusion that, under ordinary conditions, the particles of gases were separated from one another by distances great in comparison with the actual diameter of the particles, and that, for different gases, the distances between the particles were approximately the same. If these suppositions are correct, it follows that *equal volumes of all gases (at the same temperature and pressure) contain equal numbers of particles.*

Several years earlier, Dalton had considered the possibility (advanced by Gay-Lussac to explain his experimental law) that equal volumes of all gases contain equal numbers of *atoms*, whether the simple atoms of elements or the 'compound atoms' of compounds, but had rejected the idea because it was inconsistent with experimental facts. Thus when nitric oxide is decomposed into nitrogen and oxygen, 1 volume of the oxide gives $\frac{1}{2}$ volume of nitrogen and $\frac{1}{2}$ volume of oxygen. If the $\frac{1}{2}$ volume of nitrogen contains x atoms, the $\frac{1}{2}$ volume of oxygen will also contain x atoms; and if one nitrogen atom combines with one oxygen atom to form a particle of nitric oxide, there would have been x particles of the oxide. According to Dalton's provisional hypothesis, therefore, the volume of the oxide should have been the same as that of the nitrogen or the oxygen separately, viz. $\frac{1}{2}$ volume. Actually it was as great as the volume of the nitrogen and oxygen together; and since Dalton could see no way out of the difficulty he began to doubt the accuracy of Gay-Lussac's results.

Avogadro showed that the stumbling-block lay in Dalton's failure to distinguish between an *atom*, the ultimate *chemical* particle of an element, and the ultimate *physical* particle of a substance, for which the name *molecule* is now employed. By assuming that the molecule of an element might sometimes contain *more than one atom*, Dalton's problem at once becomes clear. Suppose, for example, that nitrogen and oxygen both have diatomic molecules (i.e.

molecules consisting of two atoms) then 1 volume of nitric oxide, containing x molecules each composed of 1 atom of nitrogen and 1 of oxygen, would on decomposition yield $\frac{x}{2}$ molecules of nitrogen and $\frac{x}{2}$ molecules of oxygen. The volume of each of these two gases separately, therefore, would be *half* the original volume of nitric oxide, which is in accordance with observation.

Avogadro's principle has long been universally recognized as a corner-stone of chemical science, but it is remarkable that it attained such a position only after a long interval, from its first publication in 1811 until 1858, when Avogadro's countryman, CANNIZZARO (1826-1910), by using a new approach, convinced his contemporaries of the soundness of the principle. Cannizzaro's demonstration may be summarized as follows. Let n_H and n_X be respectively the number of molecules of hydrogen and of a gaseous hydride in two equal volumes of the gases, at the same temperature and pressure. Further, let it be assumed that $n_X/n_H = A$ (Avogadro asserted that $A=1$). Then it follows that the density of the hydride, *relative to hydrogen*, is given by the expression

$$d_X = A \cdot M_X / M_H,$$

where M stands for molecular weight, referred to $H=1$; therefore

$$M_X = d_X \cdot M_H / A.$$

Cannizzaro prepared a table of known hydrides (shown below), giving in the first place the experimental values of d_X , followed by the values of $2d_X$, and lastly the results of gravimetric analyses of the hydrides *expressed as proportions in the weights* $2d_X$. The analyses could all be effected without assumption of Avogadro's principle.

TABLE OF RELATIVE DENSITIES AND MOLECULAR WEIGHTS OF GASEOUS HYDRIDES

	Hydrogen	Hydrogen chloride	Hydrogen bromide	Hydrogen iodide	Water (vapour)	Acetylene
d_X	1.0	18.25	40.5	64.0	9.0	13.0
$2d_X$	2.0	36.50	81.0	128.0	18.0	26.0
X	—	35.50	80.0	127.0	16.0	24.0
Hydrogen	2.0	1.00	1.0	1.0	2.0	2.0

	Hydrogen sulphide	Ammonia	Phosphine	Ethylene	Propylene
d_X	17.0	8.5	17.0	14.0	21.0
$2d_X$	34.0	17.0	34.0	28.0	42.0
X	32.0	14.0	31.0	24.0	36.0
Hydrogen	2.0	3.0	3.0	4.0	6.0

When it is decided to use $H=1$ as the unit for molecular weights, the true molecular weights of the hydrides must clearly contain 1, 2, 3, etc., parts of combined hydrogen: none may contain less than one part. The table shows that only the choice $M_H/A=2$ can lead to this result. Further, the table shows that the true molecular weight of gaseous hydrogen itself is 2: hence it follows that $A=1$, at least for the gases listed in the table.

In more recent years further confirmation has been given of Avogadro's principle, that *equal volumes of all gases, at the same temperature and pressure, contain the same number of molecules*, whatever the composition of the molecules may be. It has become possible to determine the number of molecules contained in the gram-molecular weight of any substance (p. 32) by several independent physical methods, which all agree in assigning a value of 6.02×10^{23} , now termed the *Avogadro number* (p. 54).

Vapour Density and Molecular Weight. The density of a gas, like that of a solid or a liquid, may be expressed in grams per c.c. or in any other similar units. It is, however, usually more important to know the densities of gases *relative to one another*, so that a standard gas must be chosen with whose density the densities of other gases may be compared. For this purpose hydrogen was selected, as being the least dense; the relative densities of all other gases would thus be greater than unity. To the relative density of a gas in terms of hydrogen, we apply the term *vapour density* (V.D.); i.e. *the vapour density of a gas is the number of times a litre of it is as heavy as a litre of hydrogen, under the same conditions of temperature and pressure*. In practice the temperature and pressure are usually taken to be 0° and 760 mm., since it is under these conditions that the weight of a litre of hydrogen has been most accurately measured.*

The *molecular weight* of a substance is the number of times its molecule is as heavy as the atom of hydrogen, taking the weight of the atom of hydrogen to be 1.008.† Molecular 'weights' are therefore *ratios or numbers*, and not actual weights.

We thus have the relation:

$$\text{Molecular Weight} = \text{Vapour Density} \times 2(1.008)$$

or, roughly, $M.W. = 2 \text{ V.D.}$

Determination of Vapour Density. In the case of a gas, the vapour density may be determined by evacuating a large globe with an

* From the V.D., the density of the gas relative to air may be obtained by dividing by 14.43, since air is 14.43 times as dense as hydrogen. Occasionally, but seldom, the term vapour density is used on the basis of $\text{air}=1$ instead of 14.43; in such cases, the V.D. relative to hydrogen can be obtained by multiplying by 14.43.

† The standard of reference for atomic and molecular weights is actually oxygen, which is arbitrarily assigned the atomic weight $O=16.0000$. On this standard, the atomic weight of hydrogen is 1.0080. For many purposes, it is a sufficiently close approximation to take $H=1$.

efficient air-pump, weighing it empty, allowing it to fill with the gas under investigation, and reweighing. The weight of a known volume of the gas at known temperature and pressure is thus obtained. The weight of the same volume of hydrogen at the same temperature and pressure may be obtained by a repetition of the process, using hydrogen; or by a calculation from the weight of one litre of hydrogen at N.T.P., which can be found in the books of reference (it is 0.0899 gm.).

To obtain reliable figures, elaborate precautions have to be taken, and even so the results obtained do not give quite accurate comparative values, since no gas *exactly* obeys the gas laws, and therefore, for actual gases, Avogadro's principle is not *exactly* true. Hence if densities are being determined for the purpose of finding molecular weights as accurately as possible, allowance must be made for this fact. The method employed is described as the method of *limiting densities*.

Although no gas strictly obeys Boyle's Law, the extent to which deviation occurs becomes less as the pressure decreases, and the law would be exactly obeyed at zero pressure. It is clearly impossible to obtain such a pressure, and the direct measurement of gas densities even at pressures closely *approaching* zero entails insuperable experimental difficulties. The problem is therefore solved in another way. Suppose that M gm. of a gas at 0° C. occupies V litres at a pressure of one atmosphere. Then its density per unit pressure in gm. per litre is $\frac{M}{V}$. At the same temperature and at a pressure of P atmospheres, its density per unit pressure would be $\frac{M}{PV}$. If the gas obeyed Boyle's Law, $\frac{M}{PV}$ would always have the same value. In practice, however, $\frac{M}{PV}$ approaches a constant value only at very low pressures, and this value is called the *limiting density* of the gas. Representing the limiting density by $\frac{M}{(PV)_0}$ and the density as determined at pressures sufficiently high for it to be measured accurately by $\frac{M}{PV}$ we see that

$$\frac{M}{(PV)_0} = \frac{M}{PV} \times \frac{PV}{(PV)_0}$$

$$\text{i.e. limiting density} = \text{density in gm. per litre at } 0^\circ \times \frac{PV}{(PV)_0}$$

In order to find the value of $(PV)_0$, PV is measured for different values of P , as low as practicable, and a curve is drawn by plotting the values of PV against the values of P . The curve is then produced or 'extrapolated' until it cuts the axis $P=0$, and the hypothetical value of $(PV)_0$ is read off. Then, for a known value of PV , the limiting density of the gas can be calculated. For example, $(PV)_0$ for nitrogen is found to be 1.00066, while 1 litre of nitrogen at 0°C . and 1 atmosphere pressure weighs 1.2504 gm. Here $PV=1$, and the limiting density is thus $\frac{1.2504}{1.00066}$ gm. per litre.

The limiting density of oxygen is $\frac{1.4290}{1.00096}$; hence since the M.W. of oxygen is 32.0000 (O_2), the molecular weight of nitrogen is $\frac{32.0000 \times 1.2504 \times 1.00096}{1.4290 \times 1.00066} = 28.007$.

Vapour Density of Volatile Liquids. The vapour density of a volatile liquid can be determined by vaporizing the

liquid and finding the weight of a known volume of the vapour at a known temperature and pressure. The principal practical methods employed for this purpose are those of DUMAS and VICTOR MEYER. The Dumas method is the more tedious, but gives more accurate results if carefully carried out with pure liquids. Victor Meyer's method is much simpler and quicker, but less accurate. Great accuracy is seldom required in this connection, so that Victor Meyer's method is usually preferred.

Victor Meyer's Method. The apparatus (of which there are many minor modifications) is shown in Fig. 15. A is a heating bath, containing a boiling liquid the B.P. of which is considerably (25° – 30°) higher than that of the liquid under investigation. This difference is necessary to ensure that the vapour of the latter liquid is produced so rapidly that it does not, during the collection of the expelled air,

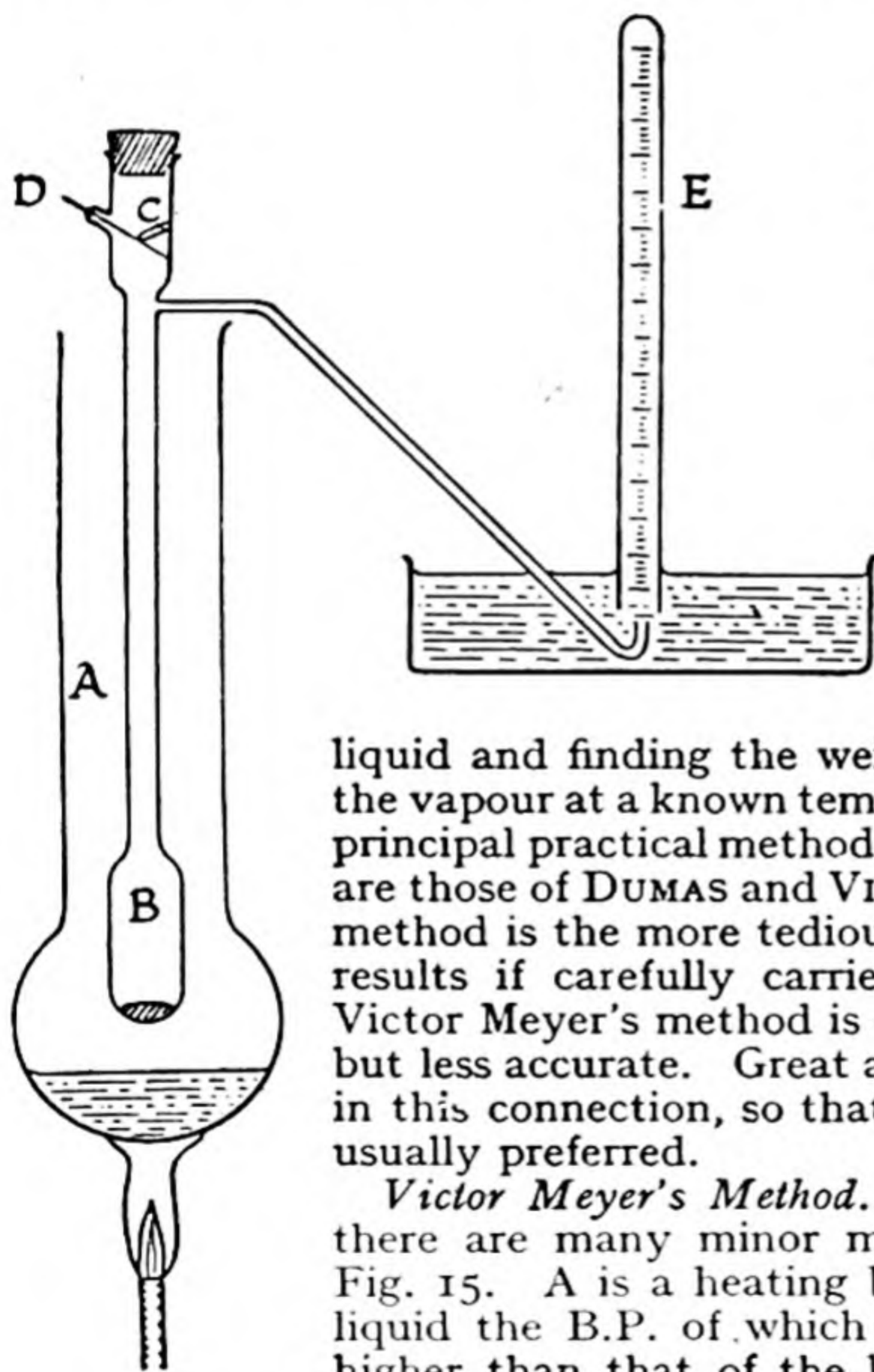


FIG. 15.
VICTOR MEYER'S
APPARATUS

appreciably mix with the air in the inner tube, B, which communicates by a side-neck to a pneumatic trough, or, preferably, with a gas-burette.

A small stoppered bottle, C, is weighed empty and is then filled with the liquid and weighed again. It is introduced into B and held in position, as shown, by a flattened glass rod, D, which is itself held by a piece of rubber tubing and can therefore be partially withdrawn when required.

When the temperature of B is steady, as shown by the fact that no more bubbles of air escape from the side-tube, the graduated tube, E, filled with water, is placed in position. The glass rod is then moved, so as to allow the small bottle to fall to the bottom of B, where a little mercury is previously placed to prevent breakage.

The liquid in the small bottle quickly vaporizes and air is displaced into the graduated tube. Since the gas laws apply to *all* gases, the volume of air collected is the same as that which the vapour would have occupied if it could have existed as vapour under these conditions. After levelling, the volume of air is read, and the barometric height and the temperature of the water in the trough are noted. The calculation may be illustrated by the following example:

0.252 gm. of a liquid displaced 29.3 c.c. air, collected over water at 16° C. 755 mm.

Vapour pressure of water at 16° C. = 14 mm.

Corrected volume of air = $\frac{29.3 \times 273 \times 741}{289 \times 760} = 27.0$ c.c. at N.T.P.

Weight of same volume of hydrogen at N.T.P. = 27×0.00009 gm.

\therefore V.D. of substance = $\frac{0.252}{27 \times 0.00009} = \underline{103.7}$.

Dumas's Method. The principle of this method is to fill a weighed glass globe with the vapour of the substance, seal it off in the flame, note the temperature and pressure, and weigh the globe again. The capacity of the globe is subsequently determined, and this completes the necessary data.

A glass globe with a long neck is weighed full of air. Some of the liquid is then introduced, and the globe is held in a heated bath at known and constant temperature (25°–30° above the B.P. of the liquid) until vapour no longer issues from the neck. The globe is then sealed, removed from the bath, dried, and weighed. Next, the tip of the neck is broken off under air-free water, which enters the globe and fills it. The globe is now dried, and, together with the bit of glass broken off, weighed again.

The difference in grams between the weight of the globe filled with

water and its weight filled with air is numerically equal to the capacity of the globe in c.c. Knowing that 1 c.c. of air at N.T.P.

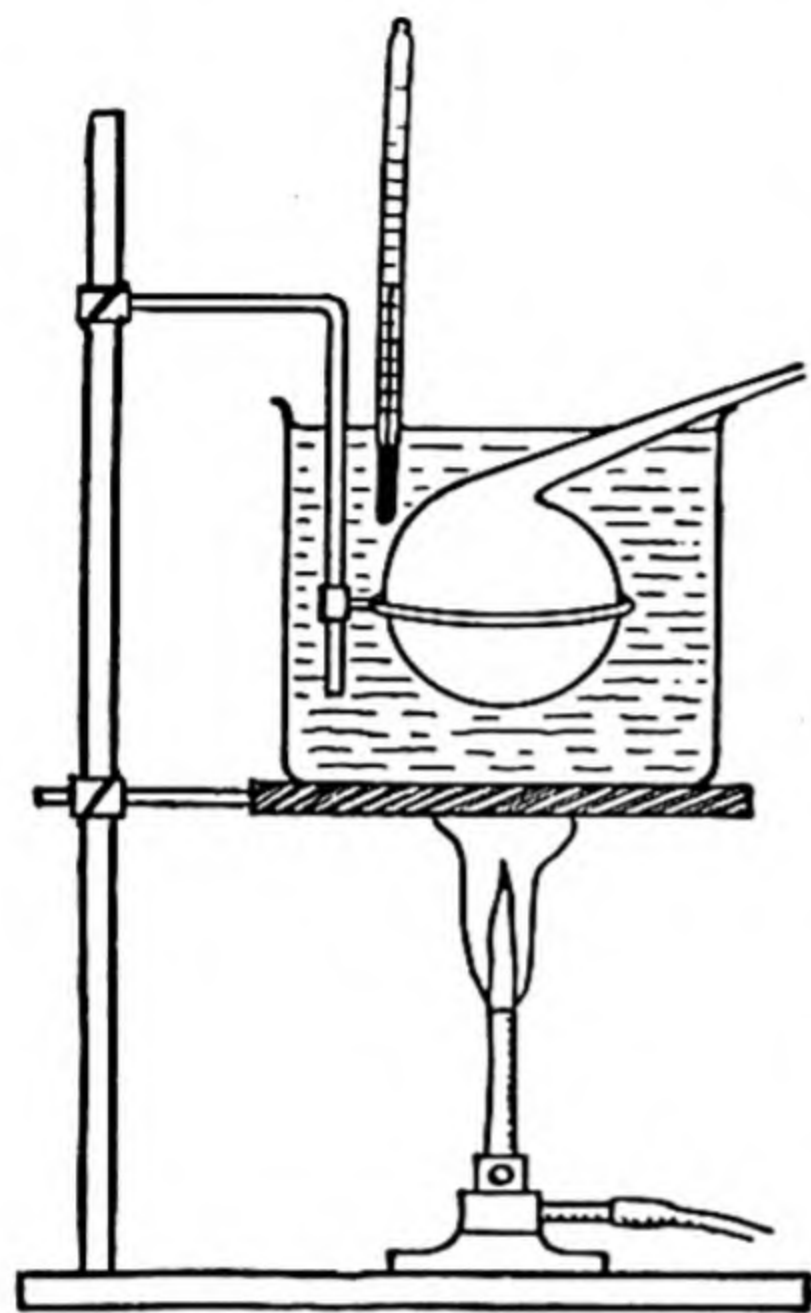


FIG. 16. DUMAS'S APPARATUS

weighs 0.00129 gm., we can therefore calculate the weight of air in the globe when it was first weighed, and hence the weight of the empty globe. This weight, subtracted from the weight of the globe when filled with vapour, gives the weight of the vapour.

The temperature is the temperature of the bath, and the pressure can be read from the barometer.

Molecular Weights in Solution. Methods of determining the molecular weights of substances in solution are described in Chapter XII.

Gram-Molecular Weight and Gram-Molecular Volume. The gram-molecular weight (G.M.W.) of a substance, is its molecular weight in grams. For example, the molecular weight of oxygen is 32; its G.M.W. is 32 *grams*. The gram-molecular volume (G.M.V.) of a gas is the volume occupied by its G.M.W. Since the gram has

long been the universal unit of mass in chemistry these terms are often abbreviated to *molar weight* and *molar volume* respectively. If gases behaved exactly according to Avogadro's principle the molar volumes at N.T.P. of all gases would be the same. Further, if, when stating the general gas law $PV/T = \text{a constant}$ (p. 24), it were understood that molar weights of gases were concerned, the constant would assume the same value for all gases, and could be assigned the symbol R . The gas law in the form $PV = RT$ thus incorporates not only Boyle's and Charles's laws but also Avogadro's principle.

The molar volumes in litres at N.T.P. of some common gases, found by dividing the molar weight of each gas by its density (gm./litre) determined at N.T.P. are as follows:

Hydrogen	22.43	Carbon dioxide	22.08
Oxygen	22.39	Ammonia	22.08
Nitrogen	22.40	Sulphur dioxide	21.89

If, however, we use in the calculation the *limiting densities* (p. 29)

the same molar volume, viz. 22.41 litres, appears for all the gases. This is evidently the molar volume at N.T.P. of an imaginary, *ideal* gas strictly obeying the gas law $PV=RT$. From the data given it will be seen that hydrogen, oxygen, and nitrogen closely approach the behaviour of such an ideal gas.

Evaluation of the Ideal Gas Constant R . Since the product PV has the dimensions (force/area) \times volume, that is, force \times length, the gas constant $R=PV/T$ must be expressed as *energy per degree*. Its numerical value depends on the units chosen for energy and for P and V .

At N.T.P.

$$P=1 \text{ atmosphere, or } 1.013 \times 10^6 \text{ dynes/cm.}^2,*$$

$$V=22.41 \text{ litres, or } 22,410 \text{ cm.}^3,$$

$$T=273.16^\circ,$$

whence R may be calculated as follows:

P	V	
atmospheres	litres	0.08205 litre-atm./degree
dynes/cm. ²	c.c.	8.314×10^7 ergs/degree
		8.314 joules/degree
		1.986 calories/degree

The value in calories per degree is obtained by taking the mechanical equivalent of heat as 1 calorie = 4.186 joules. In solving a problem in which real gases are assumed to obey the ideal gas law it is of course essential to express R in the units appropriate to the problem.

The Molecular Volumes of Liquids and Solids. Unlike the molar volumes of gases under the same physical conditions, those of liquids and solids (expressed as molar weight/density in gm./c.c.) are highly specific. In a gas under moderate pressure the average intermolecular spacing is so much greater than the molecular dimensions (p. 57) that the size, shape, and constitution of the molecules have only a small influence on the molar volume of the gas. These factors, however, assume a controlling influence when the molecules are densely packed in the liquid or crystalline state. Before the application in recent years of such powerful methods as X-ray or electron diffraction (p. 49) and infra-red spectroscopy, the comparison and correlation of molecular volumes of liquids was the principal and most promising means of investigating molecular constitution.

* The density of mercury is 13.59 gm./c.c. and the acceleration of gravity is 981 cm./sec.²; hence 1 atmosphere, or 76 cm. of mercury, is $76 \times 13.59 \times 981$ C.G.S. units, or 1.013×10^6 dynes/cm.²

Applications of Molar Weights. A knowledge of molar weights is essential in quantitative chemical operations such as those of volumetric analysis. A *molar solution*, most often but not necessarily in water, contains a molar weight of dissolved substance per litre of *solution*. The capacity of the graduated flask needed to prepare such a solution can only be exactly correct at the temperature of graduation (usually 18° or 25°), which is always engraved on the flask as well as the capacity at that temperature. Even if care is taken to prepare the solution at this temperature a subsequent change will expand or contract its volume and it will cease to be an accurately molar solution. When, in work of moderate accuracy, the temperature at which the solution is made and used does not differ widely from that specified on the flask, the inaccuracy may be disregarded; but in work of higher precision *molal solutions*, which contain a molar weight dissolved in 1 *kilogram* of *solvent*, are preferred. In preparative chemistry molar weight plays the role of 'reacting weight': reactions prescribed by chemical equations cannot be made 'operational' without a knowledge of the necessary molar weights. In many preparations and quantitative operations it is advantageous or even necessary to use an 'excess' of a reagent, which means a larger number of molecules than appear in the chemical equation: here again unless molar weights are available the work can only be conducted by a tedious and wasteful process of trial and error.

CHAPTER IV

ELECTROLYSIS

Electrolysis. An *electrolyte* is a substance which, in the liquid or dissolved state, will conduct an electric current and is decomposed by it. The decomposition is described as *electrolysis*, and the vessel in which it is carried out is called an *electrolytic cell* (or a *voltameter*). The plates or rods used for conveying the current into and out of the electrolyte are the *electrodes*. The electrode connected to the positive terminal of the electrical supply (battery, accumulator, D.C. generator) is the *anode* (+), while that connected to the negative terminal is the *cathode* or *kathode* (-).

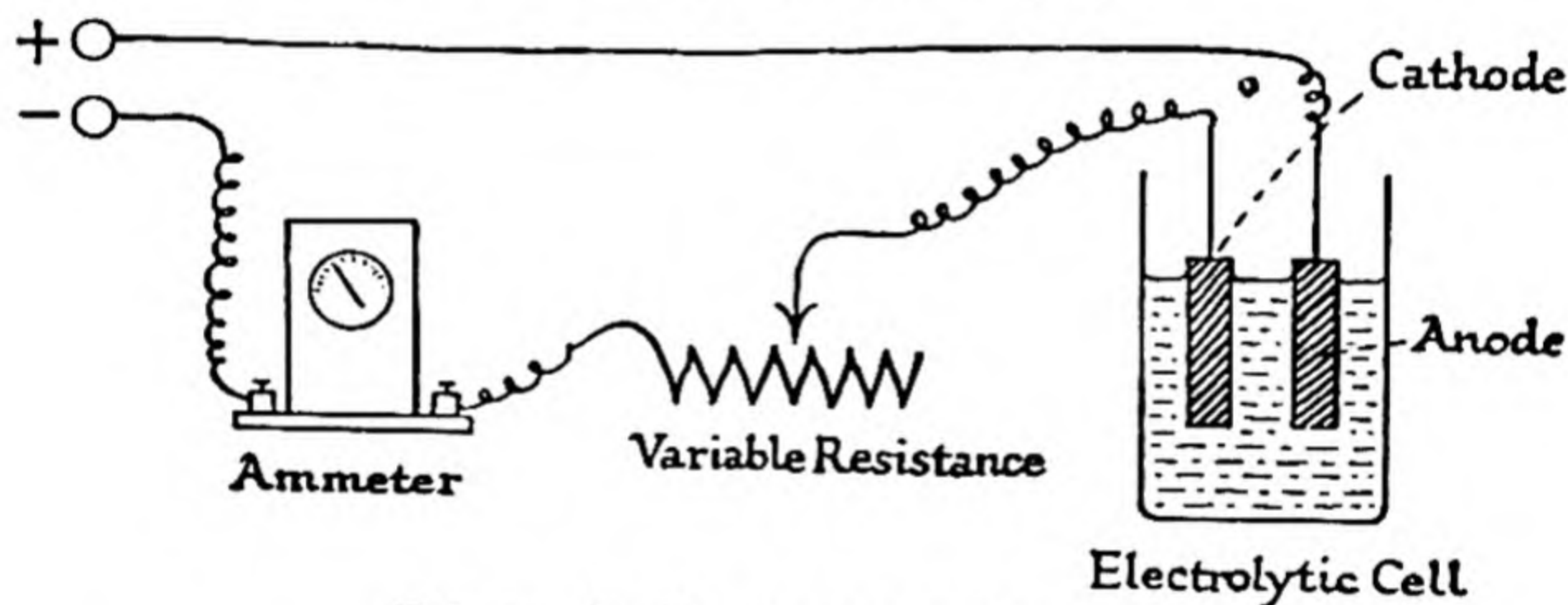


FIG. 17. AN ELECTROLYTIC CIRCUIT

Electrolytes and Non-Electrolytes. Good or 'strong' electrolytes include most salts, strong bases such as sodium hydroxide and potassium hydroxide, and strong acids such as hydrochloric acid, nitric acid, and sulphuric acid. Aqueous solutions of these substances conduct the current well, and many of them are conductors in the fused anhydrous state. Weak acids, such as acetic acid and formic acid, weak bases, such as ammonia, and a few salts, such as mercuric chloride, are poor or 'weak' electrolytes; i.e. under comparable conditions they do not conduct the current as readily as strong electrolytes do. Metals (including mercury), metallic alloys, and gas-carbon, are conductors, but since they are not decomposed by the current they are not electrolytes. Alcohol, sugar, urea, and the great majority of organic compounds are neither electrolytes nor conductors.

Faraday's Laws. When very dilute sulphuric acid is electrolysed, using platinum electrodes, hydrogen is evolved at the cathode and oxygen at the anode; under similar conditions a solution of copper sulphate will yield oxygen at the anode while the cathode receives a deposit of metallic copper. Electrolysis of concentrated hydrochloric acid, using carbon electrodes to avoid corrosion by chlorine, results in the liberation of hydrogen at the cathode and chlorine at the anode. Substances like hydrogen and the metals, which appear at the cathode during electrolysis, are said to be *electropositive*; those such as oxygen and chlorine, which appear at the anode, are *electronegative*.

Since, during the passage of the current, there is a continuous formation of products at the electrodes but no apparent chemical action in the other regions of the electrolyte, it may be assumed that there is a movement of particles of electropositive substance towards the cathode and of particles of electronegative substance towards the anode. This movement must be caused by electrostatic attraction, and therefore the moving particles must themselves be charged, each with



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FIG. 18. M. FARADAY

a charge of opposite sign to that of the electrode towards which it moves. FARADAY (1791–1867), to whom the discovery of the fundamental laws of electrolysis is due, called these charged particles *ions* (Greek *ion*, neuter present participle of *ienai*, to go), a name suggested to him by the then Master of Trinity College, Cambridge, WILLIAM WHEWELL (1794–1866). Ions which proceed to the anode are *anions*; those which proceed to the cathode are *cations*.

It is reasonable to assume that the ionic particles are charged atoms or radicals. Those in a solution of hydrogen chloride would then be positively charged hydrogen atoms (cations), and negatively charged chlorine atoms (anions). In copper sulphate solution, the ions would be copper cations and sulphate (SO_4) anions; in sodium nitrate solution, sodium cations and nitrate (NO_3) anions; and in

ammonium sulphate solution, ammonium (NH_4) cations and sulphate (SO_4) anions. However, Faraday and most of his contemporaries were cautious in admitting the existence of compound ions, such as sulphate, SO_4^{2-} , and nitrate, NO_3^- , which had no uncharged chemical counterparts.

In the course of his researches upon electrolysis, Faraday established the following laws:

FIRST LAW. The chemical action of a current of electricity is in direct proportion to the absolute quantity of electricity which passes (1832), expressed now in the form: *The mass of any individual product liberated in electrolysis is directly proportional to the quantity of electricity which has been passed through the electrolyte.*

Quantity of electricity' is measured in *coulombs*. A coulomb is the quantity of electricity required to liberate 0.001118 gm. of silver in an electrolytic cell. A current which delivers one coulomb per second is said to have a magnitude of one *ampere*. Hence the quantity of electricity passed in a circuit may be found by multiplying the *amperage* of the current by the number of *seconds* for which it has been flowing; the product gives the number of coulombs delivered. Thus a current of 2 amps. flowing for 3 minutes will deliver $2 \times 3 \times 60 = 360$ coulombs.

Faraday showed that if a current of a amps. flowing through an electrolyte for t seconds liberated w gm. of a certain product, then a current of a amps. flowing for $2t$ seconds would liberate $2w$ gm. of the product; or, in general, $w \propto at$.

SECOND LAW. For a constant quantity of electricity the amount of electrochemical action is always equivalent to a standard chemical effect founded upon ordinary chemical affinity (1833), expressed now in the form: *The masses of various products liberated in electrolysis by the passage of the same quantity of electricity are in the exact ratio of their chemical equivalents.*

Equivalents. Chemical analysis of water, copper (cupric) oxide, and iron (ferric) oxide proved that in water unit mass of hydrogen is combined with 7.94 of oxygen in the same units of mass: in copper oxide 31.53 units of copper and in iron oxide 18.81 units of iron are united with 7.94 units of oxygen. By similar means 35.2 units of chlorine are found to be combined with unit mass of hydrogen in hydrogen chloride, and 107.1 units of silver with 35.2 units of chlorine in silver chloride. It therefore appeared that in chemical 'affinity' 7.94 units of oxygen, 35.2 of chlorine, 107.1 of silver, 31.53

of copper, and 18.81 of iron are all *equivalent* to one unit of hydrogen. Consequently such numbers were termed the *equivalents* of these elements. The determination of equivalents is dependent only upon the practical accuracy of chemical analysis, and not at all upon any atomic theory or system of atomic weights. Because of their entirely empirical character, equivalents took on, in the eyes of most chemists of the first half of the nineteenth century, the importance since accorded to atomic weights, after Cannizzaro had reinstated Avogadro's principle (p. 27).

When it is accepted that each of the compounds mentioned is formed by the union of definite small numbers of atoms of the elements concerned, then it must follow that their atomic weights (in terms of $H=1$) are their equivalents multiplied by a small whole number (1, 2, 3, etc.). The work of Dulong and Petit in 1819 on the specific heats of the elements (p. 44), and that of Mitscherlich in 1821 on isomorphism (p. 45), had by Faraday's time already shown that the atomic weights of silver, copper, and iron were very probably 107.1×1 , 31.53×2 , and 18.81×3 respectively: Dumas's evidence (1833) that in organic compounds chlorine replaces hydrogen atom for atom and that oxygen replaces two atoms of hydrogen suggested that for chlorine atomic weight and equivalent are equal, and that the atomic weight of oxygen is 7.94×2 .

By its definition as the atomic weight in grams the *gram-atomic weight* of any element must contain the same number of atoms as one gram of hydrogen (when $H=1$ is the standard of atomic weights). If this number is n then the *gram-equivalents* of chlorine, silver, oxygen, copper, and iron contain respectively n , n , $n/2$, $n/2$, and $n/3$ atoms of these elements. Faraday proved that the quantity of electricity required to liberate (at a cathode) one gram-equivalent of silver, also liberated one gram of hydrogen, and the gram-equivalents of copper and iron: and, at an anode, the gram-equivalents of chlorine or oxygen. It must follow that if an ion of hydrogen is represented as H^+ those of the other elements are correctly symbolized as Ag^+ , Cu^{2+} , Fe^{3+} , O^{2-} , Cl^- . The coulomb being defined in terms of silver deposited (see above) the number of coulombs liberating the gram-equivalent of any element ($O=16.000$) is $107.88/0.001118=96,500$, a quantity appropriately termed the *faraday* (symbol F). The mass of an element liberated by one coulomb, which is $[(\text{equivalent})/96,500]$ gram, is termed its *electrochemical equivalent*.

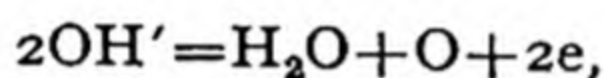
At the end of the nineteenth century it was proved that the charge upon a free *electron* equals that upon a chlorine ion, and the view could be taken that such an ion is formed by the process $Cl+e=Cl^-$, where e is an electron, and an ion of hydrogen by the loss of one electron, $H=H^++e$. Very few elementary cations are known

with charges as large as four times that on a hydrogen ion, and none with a greater charge: no elementary anions are known with charges greater than twice that on the chlorine ion. Within these limits there is a close parallelism between the *valency* of an element (p. 106) and the charge (positive or negative) on its ions.

Some Examples of Electrolysis. The more obvious phenomena of electrolysis may be illustrated by the following examples:

(i) *Water.* Pure water is a very poor conductor of electricity, a property which indicates that it contains very few ions. It does, however, contain a small proportion of hydrogen ions, H^+ , and hydroxyl ions, OH^- , and we shall see below that this fact has important consequences. In the so-called 'electrolysis of water,' it is usual to add a little sulphuric acid 'to make the water a conductor.' Actually the sulphuric acid provides hydrogen ions and sulphate ions: $H_2SO_4 \rightarrow H^+ + H^+ + SO_4^{2-}$, and it is these which carry the current. During electrolysis, the hydrogen ions travel to the cathode, where they lose their charge and are converted into ordinary hydrogen atoms; these join together in pairs to form molecular hydrogen, H_2 , which makes its appearance as hydrogen gas.

At the anode, however, sulphate ions are *not* discharged, since discharge of hydroxyl ions is easier, even though their concentration is very small:



followed by $2O \rightarrow O_2 \uparrow$.

Since the discharge of n hydroxyl ions must contribute n hydrogen ions to the liquid, and equal numbers of these two ions are discharged at each electrode, the *net* result is indeed a decomposition of water into hydrogen and oxygen, the same weight of sulphuric acid being left at the end as was added at the beginning.

(ii) *Sodium chloride.* When sodium chloride is melted, the liquid is believed to contain sodium ions, Na^+ , and chlorine ions, Cl^- , because it will conduct the current and is decomposed by it. Supposing the electrodes to be made of carbon, which is not attacked by sodium or chlorine, the result of electrolysis is the liberation of sodium at the cathode and chlorine at the anode. The positively charged sodium ions are discharged at the cathode, and form ordinary metallic sodium, while the negatively charged chlorine ions travel to the anode, lose their charge, and appear as gaseous chlorine. If the anode had been made of copper, or of some other metal attacked by chlorine, it would have been corroded, and part at least of the chlorine would not have been evolved.

In aqueous solution the cathodic product of electrolysis of common salt is usually hydrogen, but the gaseous anodic product

contains both oxygen and chlorine, the latter greatly preponderating when a concentrated solution is electrolysed. The proportion of oxygen increases as the solution is diluted with water. The explanation is that hydrogen ions, necessarily present in all aqueous solutions to a small extent, are, under most conditions of electrolysis, far more easily discharged than sodium ions: while hydroxyl ions, also necessarily present in salt solutions, are somewhat more easily discharged than chlorine ions. Owing to the withdrawal of hydrogen ions the solution around the cathode becomes alkaline during electrolysis. In concentrated *hydrochloric acid* the great excess of hydrogen ions practically completely suppresses the hydroxyl ions, and hence in this case pure chlorine appears at the anode. When *mercury* is used as the cathode in the electrolysis of sodium chloride the conditions at this electrode are greatly altered, and sodium ions are discharged, for not only can the released metallic sodium freely dissolve in mercury, but the release of hydrogen from the ionic condition at the surface of mercury is exceptionally difficult (see further, p. 249). It may here be noted that the products of electrolysis depend not only on the composition of the solution, but also upon the nature of the electrode material, and upon the electric potential differences maintained by the current between the electrodes and the solution. These potentials may often be changed by increasing or decreasing the strength of the current, so that the nature of the products may sometimes be influenced by the current strength.

(iii) *Copper sulphate*. If an aqueous solution of copper sulphate is electrolysed between platinum electrodes, it will be observed (a) that the cathode becomes covered with copper, (b) that oxygen is evolved at the anode, and (c) that the colour of the solution becomes paler and finally disappears. The solution left in the cell proves to be dilute sulphuric acid.

The explanation of these changes is quite simple. On electrolysis, copper ions travel to the cathode where they are discharged; the copper atoms then deposit themselves on the cathode, which becomes 'electro-plated.' The anodic change is the discharge of hydroxyl, as under (i) above.

If the anode of platinum is replaced by one of copper, the final result of electrolysis is the transference of copper from the anode to the cathode: the latter increases in weight to the same extent as the former decreases, and the solution remains unchanged. The difference in behaviour at the anode is due to the fact that of the three possible changes yielding electrons to the anode, (i) discharge of sulphate ions, (ii) discharge of hydroxyl ions, (iii) entry of copper *cations* into solution, the last is by far the easiest: hence in this case neither anion is discharged. The same weight of copper sulphate is

thus being formed in a given time as is electrolysed in that time, so that the total concentration of the solution is unaltered.

How this and similar explanations of electrolytic changes have to be modified, to agree with additional facts discovered later, is a subject deferred to Chapter XVI. Meanwhile, it may be pointed out that water is by no means the only solvent in which electrolytes produce conducting solutions; solutions in alcohol, liquid ammonia, acetone, and many other liquids show a similar behaviour, though in differing degrees.

Examples: (i) A current of 2 amperes is passed through a solution of nickel chloride, NiCl_2 , for 3 hours 25 minutes. What weight of nickel will have been deposited on the cathode? The atomic weight of nickel is 58.7.

The chemical equivalent of nickel in its dichloride is $\frac{58.7}{2} = 29.35$. To deposit 29.35 gm. of nickel, 96,500 coulombs are required.

2 amps. for 3 hours 25 minutes $= 2 \times 205 \times 60$ coulombs.

If 96,500 coulombs deposit 29.35 gm. nickel, then $2 \times 205 \times 60$

$$\begin{aligned} \text{coulombs deposit} & \quad \frac{29.35 \times 2 \times 205 \times 60}{96,500} \\ & = \underline{7.49 \text{ gm. nickel.}} \end{aligned}$$

(ii) In an electrolytic cell, the volume of hydrogen evolved in 56 minutes was 126.0 c.c., measured dry at N.T.P. Calculate the strength of the current.

22,400 c.c. hydrogen weigh 1.008×2 gm. at N.T.P.

\therefore 126 c.c. hydrogen weigh $\frac{1.008 \times 2 \times 126}{22,400}$ gm.

1.008 gm. hydrogen is liberated by 96,500 coulombs,

$\therefore \frac{1.008 \times 2 \times 126}{22,400}$ gm. hydrogen is liberated by

$$\begin{aligned} & \quad \frac{96,500 \times 1.008 \times 2 \times 126}{1.008 \times 22,400} \\ & = \frac{965 \times 252}{224} \text{ coulombs.} \end{aligned}$$

Coulombs = amperes \times seconds.

$$\therefore \frac{965 \times 252}{224} = x \times 56 \times 60$$

$$\therefore x = \underline{0.32 \text{ amperes.}}$$

ELECTROLYSIS

(iii) A current of 1.5 amperes was passed for 50 minutes through a solution of a metallic salt. 5.03 gm. of the metal was deposited on the cathode. Calculate the chemical equivalent of the metal.

$$\begin{aligned} 1.5 \text{ amperes for 50 minutes} &= 1.5 \times 50 \times 60 \\ &= 4,500 \text{ coulombs.} \end{aligned}$$

$$4,500 \text{ coulombs liberate } 5.03 \text{ gm. metal,}$$

$$\begin{aligned} \therefore 96,500 \text{ coulombs liberate } &\frac{5.03 \times 96,500}{4,500} \\ &= 107.8 \text{ gm. metal.} \end{aligned}$$

$$\therefore \underline{\text{Chemical equivalent of metal is 107.8.}}$$

CHAPTER V

ATOMIC WEIGHT AND SIZE

Atomic Weight Standards. Dalton's choice of the lightest element as standard for atomic weights ($H=1$) was natural and logical, but at length encountered the practical difficulty that only a minority of the elements yield *hydrides* that can be readily purified and employed in chemical analysis. On the contrary, only a very few elements fail to yield stable *oxides*, and most also yield stable *chlorides*. Through the analysis of oxides and chlorides therefore it is possible to express the atomic weights of nearly all the elements directly in terms of the atom of oxygen or of chlorine as standard. A second step involving an exact knowledge of the composition of water or of hydrogen chloride is then required to convert these atomic weights to the hydrogen standard. BERZELIUS (1779-1848), whose devoted analytical researches occupied most of his long active life, and resulted in the first comprehensive table of atomic weights, advocated the standard $O=100$, but this proposal gained little general acceptance.

It was STAS (1813-91), the principal and immediate successor to Berzelius in the field of atomic weight determination, who from about 1850 onwards successfully pressed the standard $O=16.000$ on his contemporaries. Later exact work on the composition of water (p. 282) proved that this standard implies $H=1.0080$, since 16.000 gm. of oxygen are combined with 2.0160 gm. of hydrogen in water. Stas's standard has been recognized and universally accepted up to the present day. There is, however, every likelihood that in the very near future the standard $C=12.000$ will replace the oxygen standard prevailing for the previous hundred years. The change to the carbon standard was proposed by the International Committee on Atomic Weights in 1957, and offers important advantages in the modern method of fixing atomic weight by the method of the mass spectrometer (p. 47).

Chemical Equivalents. The *equivalent* of a substance on the present standard $O=16.000$ is the number of units by weight of that substance which combine with or displace 8.0000 of the same units by weight of oxygen, or 1.0080 units of hydrogen. Since the unit of weight almost invariably used in chemistry is the gram,

the word 'equivalent,' which correctly implies a mere number or ratio, is often taken to mean gram-equivalent, i.e. the equivalent in grams.

Chemical methods of determining the atomic weight of an element were mostly based upon a careful determination of the equivalent of the element. Details of such procedure are given for hydrogen and oxygen on p. 504 and for carbon on p. 396. Typical methods of determination are:

- (i) Quantitative analysis of the *oxide* of the element, by converting a known weight of the element into its oxide and weighing again. Conversely, a known weight of the metallic oxide may be reduced and the weight of metal determined.
- (ii) By forming a *hydride* of the element and analysing it quantitatively. This has been carried out very accurately for oxygen and for chlorine.
- (iii) By quantitative analysis of the *chloride* of the element, the equivalent of chlorine (35.457) having been accurately found by method (ii).

It should be noted that, unlike the atomic weight, the equivalent of an element is not *necessarily* a constant. In the compounds nitrous oxide, N_2O , nitric oxide, NO , and ammonia, NH_3 , the equivalent of nitrogen (atomic weight 14.0) is respectively 14, $14/2$ and $14/3$; in carbon dioxide, CO_2 , and methane, CH_4 , the equivalent of carbon (atomic weight 12) is $12/4$, but in carbon monoxide, CO , and in ethylene, C_2H_4 , it is $12/2$.

Atomic Heat. At the present day, no difficulty is experienced in deciding which multiple of the equivalent of an element must be taken as the atomic weight, and in fact the atomic weights of all known elements have been determined. In earlier times, however, a good deal of uncertainty existed, and a discovery made by DULONG (1785–1838) and PETIT (1791–1820) in 1819 proved of considerable assistance. These chemists showed that, for many solid elements, the product of the specific heat and atomic weight was approximately constant, viz. 6.4. In other cases, they found that the then accepted atomic weight of an element gave a product which was a multiple of 6.4; thus the specific heat of silver (0.056) multiplied by 216—its supposed atomic weight—gives a value of 12.1, i.e. roughly twice 6.4. Dulong and Petit accordingly maintained that the atomic weight of silver could not be 216 but must be half this, viz. 108.

The product of atomic weight multiplied by specific heat is known as the *atomic heat* of the element. Dulong and Petit's rule is therefore expressed by the statement that *the atomic heat of many solid elements is approximately 6.4*. There are several excep-

tions to the rule (e.g. carbon, silicon); at high temperatures, however, the atomic heats of these elements also approach 6.4.

Example: The equivalent of iron in one of its compounds is 27.92. The specific heat is 0.105. Find its atomic weight.

$$\text{Atomic weight} \approx \frac{6.4}{0.105} = 61.$$

The nearest whole number multiple of the equivalent is $27.92 \times 2 = 55.84$.

Cannizzaro's Method. If an element forms a large number of gaseous or volatile compounds, the compounds may be analysed, and their molecular weights may be determined by a vapour density method. Supposing that many compounds are investigated, the probability is that at least one of them will contain only *one* atom of the element per molecule; hence the *smallest* weight of the element found in the gram-molecular weight of any of the compounds may—provisionally—be taken as its gram-atomic weight. For example, nitrogen forms several gaseous or volatile compounds, some of which, with the appropriate data, are shown below:

Compound	M.W. in grams	Number of Grams of Nitrogen in G.M.W. of Compound
Nitrous oxide	44	28
Nitric oxide	30	14
Ammonia	17	14
Hydrazine	32	28
Hydrazoic acid	43	42
Nitrosyl chloride	65.5	14
Methylamine	31	14

It is unlikely that, in such a varied and reasonably large number of compounds, there is no single one containing only *one* atom of nitrogen in its molecule. Hence 14 may be accepted provisionally as the atomic weight of nitrogen, and in any case the value cannot be *larger* than this.

The application of this method of Cannizzaro (1858), which was a natural corollary of his proof of Avogadro's principle (p. 26), was of great importance in the development of chemistry. Up to that time, Avogadro's principle had been neglected, and much doubt existed over the atomic weights of many elements. Cannizzaro employed the principle to calculate the molecular weights of volatile compounds, and was thus able to fix atomic weights in the way just described.

Mitscherlich's Law. The crystallographer MITSCHERLICH (1794–1863) suggested another way of determining the atomic weight of

an element. He observed that salts of similar constitution often crystallize in similar crystalline forms, i.e. they are *isomorphous* (Greek, *isos*, equal; *morphē*, form). This discovery was expressed as the *law of isomorphism*, viz.:

The same number of atoms combined in the same manner produce the same crystalline form, which is independent of the chemical nature of the atoms.*

The application of this law to atomic weight problems may be illustrated by Mitscherlich's own work on selenium. He found that potassium sulphate was isomorphous with potassium selenate, and therefore assumed that these two salts had similar constitutions. On analysis, the following figures were obtained:

Potassium Sulphate			Potassium Selenate		
per cent			per cent		
Potassium	.	44.83	Potassium	.	35.29
Oxygen	.	36.78	Oxygen	.	28.96
Sulphur	.	18.39	Selenium	.	35.75

Taking a constant weight of potassium (say 44.83 parts) in the two compounds, the weight of selenium combining with this weight is $\frac{35.75 \times 44.83}{35.29} = 45.40$.

$$\therefore \text{atomic weight of sulphur} : \text{atomic weight of selenium} \\ = 18.39 : 45.40.$$

But the atomic weight of sulphur = 32,

$$\therefore \text{atomic weight of selenium} = \frac{32 \times 45.4}{18.39} = 79.$$

This method was also employed to correct the atomic weights of chromium and vanadium.

It may be observed that isomorphism does not *always* imply similarity of chemical constitution, nor are similar substances *necessarily* isomorphous. For example, potassium perchlorate, KClO_4 , is isomorphous with barium sulphate, BaSO_4 ; and sodium nitrate, NaNO_3 , with calcium carbonate, CaCO_3 (calcite). On the other hand, potassium nitrate, KNO_3 , is not isomorphous with sodium nitrate, nor potassium chlorate, KClO_3 , with sodium chlorate, NaClO_3 .

Modern Methods. (i) Reference to the Periodic System (Chapter VIII), in which the elements are arranged (with a very few exceptions) in the order of their atomic weights, enables the factor

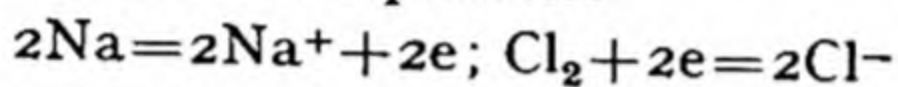
* Isomorphism is rarely exact. A rough test, suggested by Mitscherlich, is to see whether a crystal of one substance will grow in a saturated solution of the other. If so, they are isomorphous 'within the meaning of the law,' i.e. with sufficiently close approximation.

atomic weight equivalent to be settled by mere inspection, for there is only one place in the system for each individual element.

(ii) Physical methods are now available by which atomic weights may be determined directly.

Outline of Atomic Constitution. Atomic structure will be explained in more detail in Chapter IX, but a brief description is here necessary to an understanding of the operation of the mass-spectrograph, and of the modern means of assessing atomic size. Although atoms bear no net electrical charge they are constituted of electrically charged particles, which for present purposes we may take to be of two kinds: *electrons*, each identical in mass and *negative* charge in all atoms; *nuclei*, providing the *positive* charge exactly balancing the total electronic charge. The number of atomic electrons rises by steps of unity from one in hydrogen to 92 in uranium, but an atom contains only *one* nucleus, located centrally. Relative to the atomic weight standard $O=16$, the mass of an electron is only 0.00053; the nucleus therefore bears not only the total positive charge equivalent to that of the electrons, but also almost all the mass of the atom. Unlike electrons, nuclei are specific in mass and charge to each atom.

In many chemical reactions electrons are transferred from one atom to another. Thus the equations



express the interaction of sodium with chlorine. Sodium atoms become *positive ions*, or *cations*, and the chlorine atoms *negative ions*, or *anions*. The product, sodium chloride, necessarily consists of equal numbers of these ions. Electrons can be freed from atoms, and their properties studied, by such simple means as is used in all thermionic valves, viz. heating a metallic filament. Being electrically charged they can be given high velocities and kinetic energies by passage through an electric field (again as in a thermionic valve). In a magnetic field they move in a curved path round the direction of the field.

The Mass-spectrograph. In collisions between electrons (given sufficient kinetic energy) and molecules, electrons are expelled from the latter, which thereby suffer partial or complete decomposition, resulting in the production of positive ions from their constituent atoms or other fragments. The mass-spectrograph operates by separating, collecting, and identifying such fragments.

Electrons from a suitable source (e.g. a heated filament as in a thermionic valve), accelerated by an electric field and collimated into a beam by a system of slits, pass through a gas at low pressure (10^{-4} – 10^{-7} mm. of mercury). The positively charged fragments

so produced are then filtered from the electrons by a combination of magnetic and electric fields, the latter imparting a high and nearly uniform velocity to the positive ions. These now pass through a slit into a second highly evacuated chamber, where they come under the influence of a strong magnetic field perpendicular to their direction of motion (Fig. 19). The constituents of the beam of ions are rotated in semicircles of radii depending on the ratio of charge to mass $\frac{e}{m}$. Ions of equal charge are thus separated into a 'mass spectrum' which may be permanently recorded as a series of lines by allowing the ions to impinge on a photographic plate.

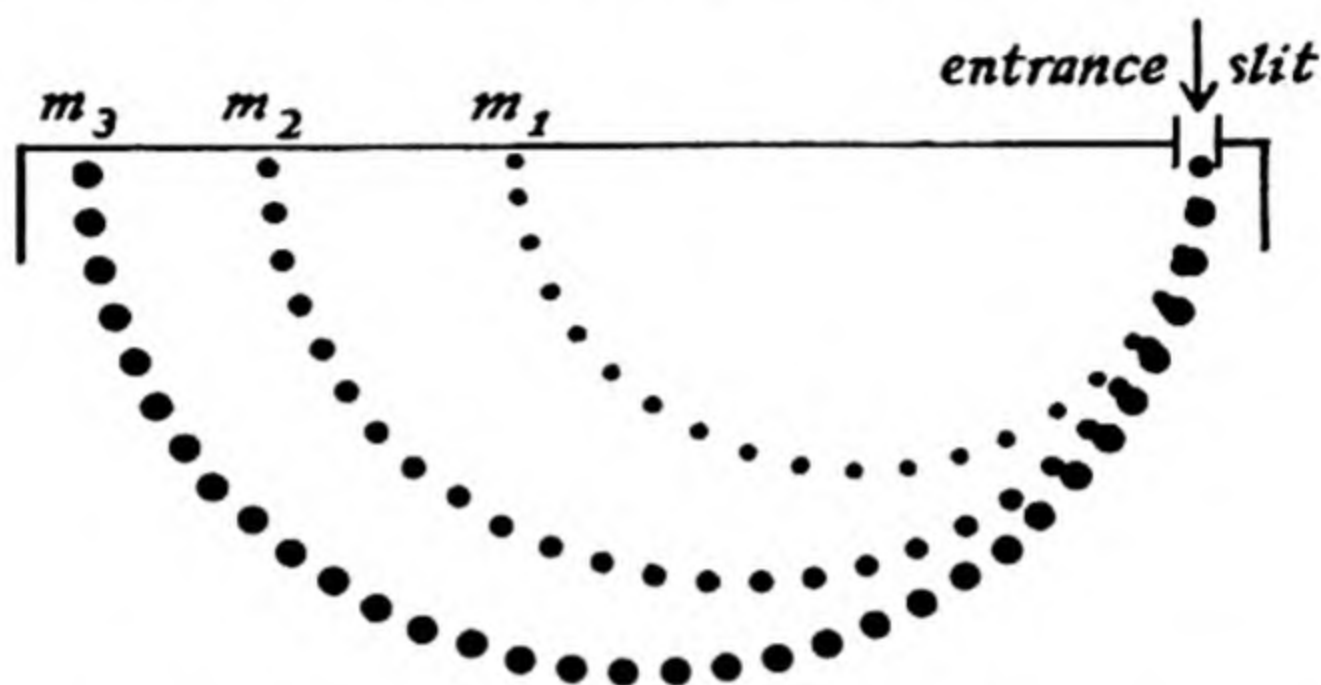


FIG. 19. THE MAGNETIC SEPARATION OF POSITIVE IONS WITH EQUAL CHARGE AND VELOCITY BUT DIFFERENT WEIGHTS. (THE MAGNETIC FIELD IS PERPENDICULAR TO THE PAPER.)

Such a type of instrument is capable of comparing atomic masses directly in one operation, and thus avoids the series of quantitative experiments, with their attendant errors, usually needed in the classical chemical methods. As will be shown later (p. 98), the atoms of an element are not all equal in mass as Dalton supposed, but consist of groups of *isotopes*, of differing natural abundance. The mass-spectrograph separates these different but chemically identical forms; and by careful examination of the 'mass spectrum' their relative abundances can be determined. The 'chemical' atomic weight is the weighted mean of the isotopic masses. In recent years the determination of atomic weight by such powerful means has reached a very high degree of refinement, and nearly all the numerous corrections of atomic weights in the past decade have been based on such determinations. An instrument with very exact electrical means of estimating isotopic abundances is usually termed a 'mass-spectrometer.'

Atomic Size: the Diffraction of X-rays by Crystals. Accurate estimates of atomic size were not achieved before the discovery in 1912 of the diffraction of X-radiation by crystals (by Friedrich and Knipping at the suggestion of VON LAUE (1879-1960)), although its order of magnitude (10^{-8} cm.) had been established earlier. The application of X-ray diffraction was brilliantly exploited by SIR W. H. BRAGG (1862-1942) and his son, now SIR LAWRENCE BRAGG.

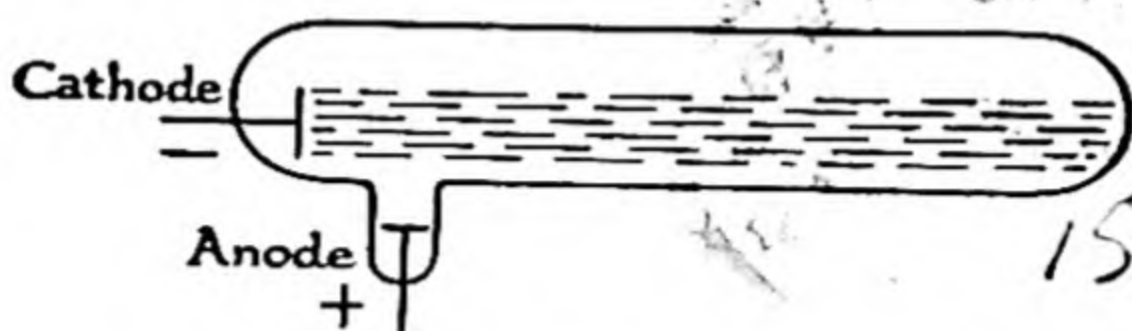


FIG. 20. CATHODE RAYS

X-radiation, emitted from a metallic target fixed across the track of 'cathode rays' developed in a gas-discharge tube (Fig. 20), was discovered in 1895 by VON ROENTGEN (1845-1923). Two years later J. J. THOMSON (1856-1940) demonstrated that a beam of cathode rays behaved like a stream of fast-moving *electrons* each with a negative charge equal to that upon a chloride ion, Cl^- , but with a mass only a small fraction ($\frac{1}{1840}$) of that of a hydrogen atom. Within the next decade the so-called *alpha* and *beta* 'rays' emitted spontaneously by radioactive atoms, such as radium, were also explained as fast-moving particles, the *beta* type being again electrons (p. 97). This being therefore a time when 'rays' were apt to turn into high-speed 'particles,' it was confidently expected that X-rays would prove no exception. W. H. Bragg, until finally convinced to the contrary by Friedrich and Knipping's discovery, was indeed a foremost supporter of the 'corpuscular' theory of X-radiation.

In more recent years the wave-length of X-radiation has been accurately determined by the classical method of the optical ruled grating adapted to the very short wave-lengths concerned. By this means it has been shown that the wave-length depends entirely on the metal used as target for electron bombardment:

Target	Atomic weight	$\lambda \times 10^8$ cm.
Chromium	52	2.289
Copper	63.5	1.541
Molybdenum	96	0.713

These wave-lengths may be compared with those of visible light, from about $7,000 \times 10^{-8}$ cm. in the red, to about $4,500 \times 10^{-8}$ cm. in the violet.

The interaction with a crystal of X-radiation of uniform wave-length (called *monochromatic* in analogy with visible light) is explained in Fig. 21. The centres of the atomic units composing

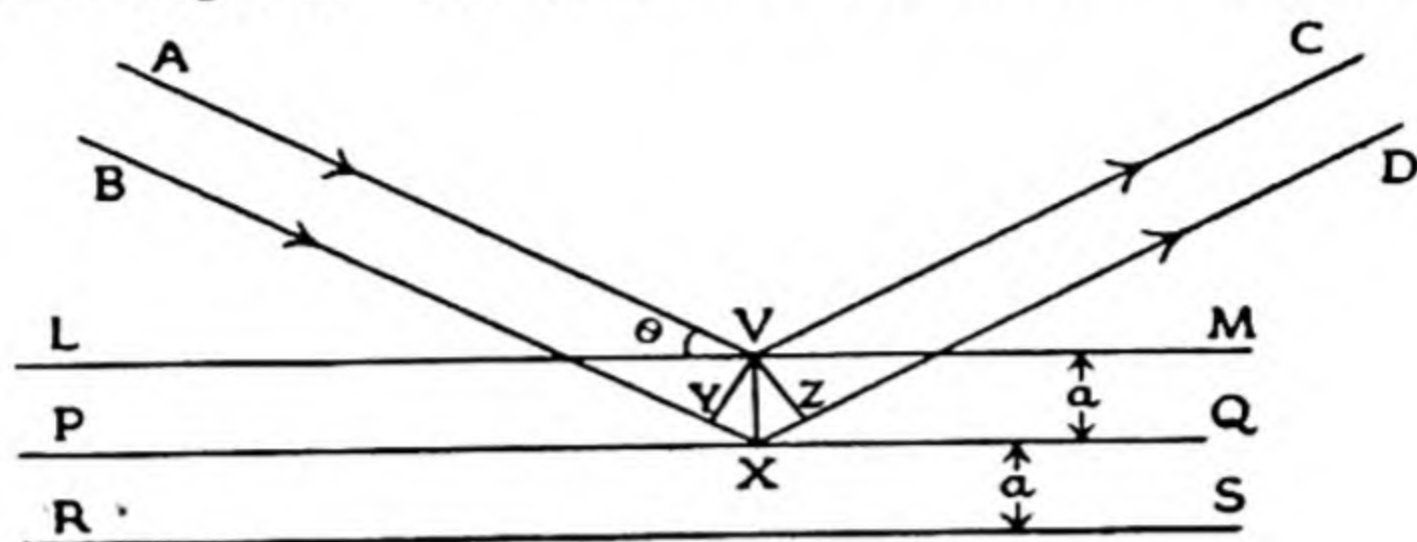


FIG. 21. DIFFRACTION OF X-RAYS

the crystal lie in the equidistant layers represented edgewise by the lines LM, PQ, and RS. The paths of two rays A and B out of a parallel beam impinging at the glancing angle θ on the crystal surface are shown by the tracks AVC and BXD. Unlike visible light, X-radiation can penetrate to layers below the surface before being reflected (as along XD). VY and VZ are perpendicular to the incident and reflected rays respectively. Between the rays AVC and BXD there is a difference $YX + ZX$ in path length. From the figure we see that since $\angle YVX = \angle ZVX = \theta$, $YX + ZX = 2a \sin \theta$. If λ is the wave-length of the radiation the reflected rays reinforce each other only when the angle θ is so adjusted that the path difference is an integral number of wave-lengths, $n\lambda$.

$$\text{Hence } n\lambda = 2a \sin \theta.$$

This simple relation, between the wave-length λ , the 'spacing' a in a crystal, and θ the angles of strong reflection, appropriately known as Bragg's law, is the basis of all X-ray crystallography. It enables the spacing a to be calculated from observations of θ when λ is known. Since $\sin \theta$ cannot exceed unity we notice that no such reflection can take place unless $\frac{n\lambda}{2a}$ is less than unity: that is, unless

the wave-length λ is comparable with the crystal spacing. The fact that such reflection did occur and obeyed Bragg's law gave the first evidence that X-radiation, like light, has the properties of a wave-propagation, and that its wave-length is of the order 10^{-8} cm.

In the original X-ray spectrometer (Fig. 22) devised by Sir William Bragg and his son the strong reflected beams were detected by their power of ionizing, i.e. rendering electrically conducting, the air in an ionizing chamber into which they passed. The crystal was mounted on a turn-table so that the effect of different angles of incidence could be conveniently observed. In a modern X-ray

'camera' the ionizing chamber is replaced by a photographic film set cylindrically round the crystal, which is slowly rocked by mechanical means through a small angle. The film on development yields a 'rotation photograph' for the crystal. To secure all its characteristic spacings it may be necessary to take several such photographs with the crystal set up in the camera in different aspects. A *crystal powder*, in which all the crystal faces are exposed at random to the radiation, can also be made to yield serviceable 'powder photographs.'

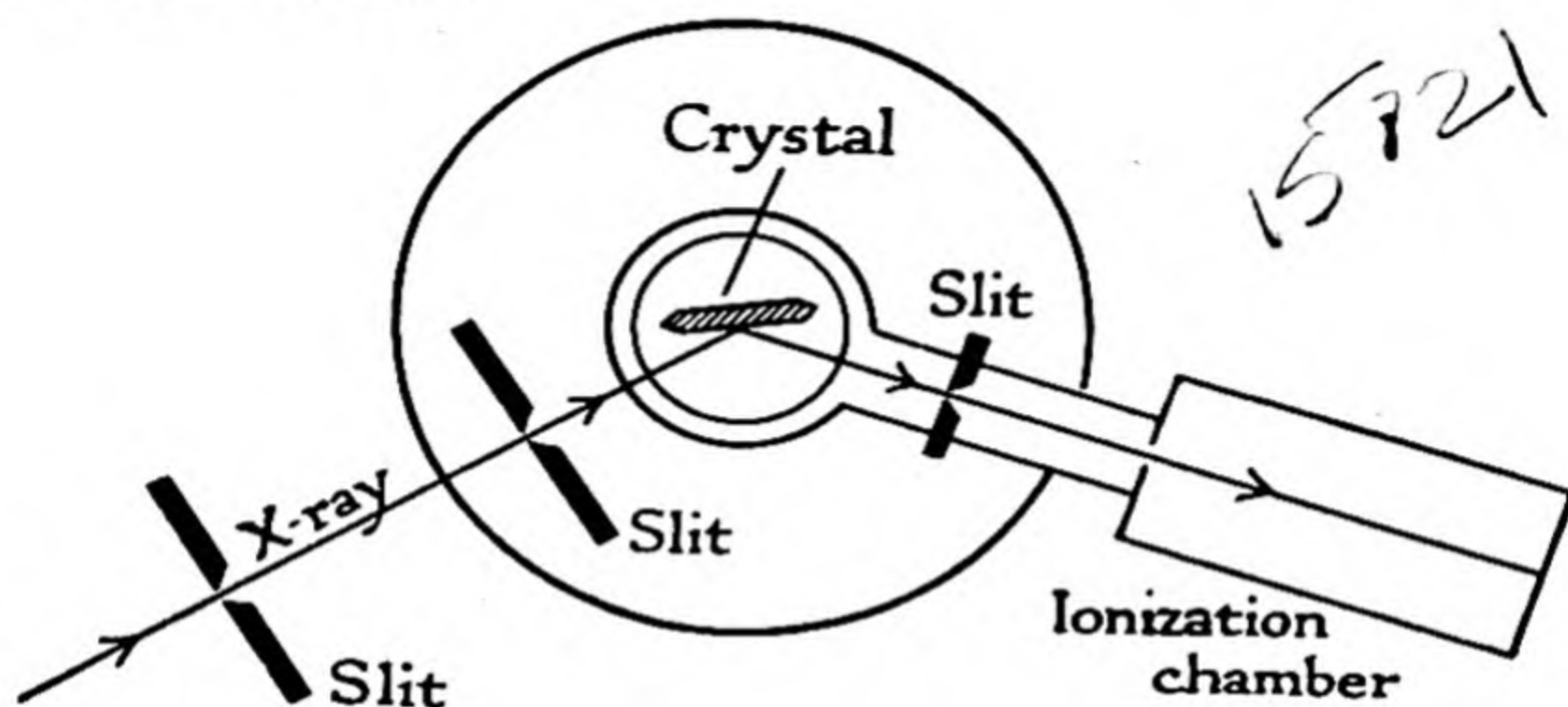


FIG. 22. THE X-RAY SPECTROMETER

The Diffraction of 'Particles.' In the experiments of 1912 von Laue was solely concerned to discover the nature of X-radiation. Although neither he nor his contemporaries could then have foreseen the vast flood of knowledge about the solid state which was to flow from his crucial experiment, it was universally held to exclude finally a 'particle' nature for X-radiation, just as much earlier the study of the diffraction of visible light was considered to exclude the Newtonian corpuscular hypothesis.

In the years between 1927 and 1932 the discovery that a stream of light particles moving in parallel tracks could be substituted for the X-ray beam (as in Fig. 22), and likewise underwent diffraction, reopened this question. The particles may be electrons, protons (hydrogen ions, H^+), α -particles (helium ions, He^{2+}), or neutrons (uncharged particles of mass nearly equal to that of a hydrogen atom, p. 97). The 'wave-length' associated with the particle (determined by applying Bragg's law) is always inversely proportional to its momentum mv in the impinging beam. It would be out of place here to enlarge upon the revolution in the theories of classical physics set off by these discoveries, which has resulted in

the whole new science of 'wave mechanics' (see also p. 91), but some of the practical consequences are of great value in chemistry.

Similarly to the diffraction of X-radiation by a crystal powder, electrons are measurably diffracted by the molecules in a gas, and from this phenomenon a bulk of knowledge about the structures of gaseous molecules has been gained complementary to that provided by X-ray diffraction for solids. While in an object viewed by an optical microscope two points closer together than the wave-length of visible light (10^{-5} cm.) cannot be 'resolved,' an *electron microscope*, working on wave-lengths of the order 10^{-8} cm., can resolve nearly down to molecular dimensions. Neutron diffraction, the latest development of diffraction methods, is filling in much of the detail of the structure of solids obscured in X-ray diffraction.

Crystal Structure. Early in the history of crystallography it had been accepted that the geometrical forms so characteristic of crystals can only result from a regular and uniform distribution of their chemical units (whether atoms, ions, or molecules) at the points of a three-dimensional network or *space lattice*. By the time the discovery of X-ray diffraction brought their work into immediate practical use mathematicians (especially BRAVAIS, 1811-63) had proved that there exist only a strictly limited number of distinct space lattices, each with its spacings and characteristic numerical relations between them. With such a well-established body of knowledge at disposal the study of crystal structure by X-ray diffraction made very rapid progress. It is usually possible to deduce from 'rotation photographs' the type of lattice on which the crystal is built. One of the first results was the structure of sodium chloride seen in Fig. 29. It must be realized that in such diagrams the small spheres merely indicate the *centres* of atoms (or ions), which are actually in contact.

Use of the Ångström Unit. Atomic and molecular dimensions are now conveniently expressed in terms of the unit of length 10^{-8} cm., first employed by the Swedish spectroscopist J. A. ÅNGSTRÖM, who in his map of the solar spectrum (1868), achieved the first accurate measurements of the wave-lengths of visible light, and expressed them in this unit of length, which in commemoration is named the *Ångström* (symbol Å):

<i>Atomic Units</i>	<i>C.G.S. Units</i>	<i>Name and symbol</i>
Length	10^{-8} cm.	1 Ångström, Å
Area	10^{-16} cm. ²	1 square Ångström, Å ²
Volume	10^{-24} cm. ³	1 cubic Ångström, Å ³

Atomic Radii. In the crystals of most metals their spherical atoms are packed as closely as possible, in a structure well adapted for the observation and interpretation of the spacings, and thence of the distances between the centres of atoms in contact. The atomic radii, *defined as half these distances*, of some common metals are shown below:

<i>Series in the Periodic System</i>		<i>Atomic radii (Å.)</i>					
I	Li	Be					
	1.52	1.12					
II	Na	Mg	Al				
	1.86	1.60	1.43				
III	K	Ca		Cr	Fe	Cu	Zn
	2.31	1.96		1.25	1.24	1.28	1.32
IV	Rb	Sr				Ag	Cd
	2.47	2.15				1.44	1.48
V	Cs						Pb
	2.63						1.75

The range of size is narrow, the largest atom, Cs, having little more than twice the radius of the smallest.

To the above metallic radii may be added the following radii of some non-metals, also defined as half the distance between centres of atoms in the elementary forms or compounds indicated:

H(H ₂)	C (diamond)	N (hydrazine, N ₂ H ₄)	O (hydrogen peroxide)
0.37	0.77	0.74	0.73
Si (crystalline silicon)	P (white phosphorus)	S (rhombic sulphur)	
1.17	1.10	1.06	

All the atomic radii listed are 'combining radii,' that is, half the distance between chemically-linked like atoms. No other meaning can now be attached to the term atomic radius, since an isolated atom has no well-defined boundary.

Gram-ionic and Gram-formula Weights. For elements that form elementary ions, e.g. Cl⁻, Mg²⁺, gram-ionic and gram-atomic weights are equal, since the change in weight on gain or loss of electrons is quite negligible. Similarly the gram-ionic weight of a compound ion is the sum of the gram-atomic weights contained in it: e.g. the gram-ionic weight of sulphate, SO₄²⁻, is 32.00 + 64 = 96.00. A salt, such as sodium chloride or magnesium sulphate, is an assemblage of equal numbers of positive and negative ions (Na⁺,

$\text{Cl}^- : \text{Mg}^{2+}, \text{SO}_4^{2-}$). Therefore while the formulae NaCl and MgSO_4 cannot represent actual molecules they do accurately express the chemical *composition* of the salt crystals. Thus the sums of gram-ionic weights $23 + 35.47 = 58.47$ and $24.32 + 96.00 = 120.32$ are respectively the *gram-formula weights* (G.F.W.) of the two salts. Although the usage cannot now be justified, gram-formula weights are often called gram-molecular weights.

The Avogadro Number. According to Avogadro's principle the number N of molecules in any molar weight is a universal constant, now termed the *Avogadro number*. From N molecules of a compound such as hydrogen chloride we can by suitable means obtain N atoms of hydrogen and N atoms of chlorine or alternatively N hydrogen ions (H^+) and N chlorine ions (Cl^-). It follows that the same constant N is the number of atoms in a gram-atom or the number of ions in a gram-ion. From the crystal structure of diamond elucidated by X-ray diffraction it is found that one atom of carbon is contained in a cube of side 1.7834×10^{-8} cm. (at 23.5°C). Hence the volume of the crystal containing one atom is $(1.7834)^3 \times 10^{-24}$ c.c. The atomic weight of carbon is 12.011, and the density of diamond at 23.5°C is 3.5184 gm./c.c., so the volume of diamond containing N atoms is $\frac{12.011}{3.5184}$ c.c. at that temperature.

$$\begin{aligned} \text{Hence } N &= \left(\frac{12.011}{3.5184} \right) \div (1.7834)^3 \times 10^{-24} \\ &= \underline{6.024 \times 10^{23}}. \end{aligned}$$

The molar weight of an ideal gas at N.T.P. occupies 22,410 c.c. (p. 33). Hence the number of molecules per c.c. under these conditions is

$$\frac{(6.024 \times 10^{23})}{22,410} = \underline{2.69 \times 10^{19}}$$

The description 'Avogadro number' is of honorific and not historical significance, for Avogadro himself could not in his time have envisaged any possibility of evaluating it. The title 'Avogadro's number' is therefore incorrect, though often used.

A *mole* is a quantity comprising N particles, which may be molecules, atoms, ions, or even electrons. The term is applicable either to pure substances or to homogeneous mixtures (solutions) of them, and it is in this latter respect that it is most useful. The N -particles in a mole of a mixture of pure substances A and B are composed of $x_A N$ particles of A and $(1 - x_A)N = x_B N$ of particles of B. The fractions x_A and x_B are known as the *mole fractions* of A and B respectively, and it is in terms of such fractions that the

composition of a solution is most informatively expressed. The term *mole* has a wider applicability than molar weight, and the two terms should not be confused.

Other Methods of Evaluating the Avogadro Number. Before the application in 1954 of the crystal analysis described above, which leads to the most accurate determination of the Avogadro number, its value was based upon older methods:

(a) 1911: Atoms of the radioactive metal radium spontaneously eject rapidly moving, positively charged helium atoms, which can be individually counted by physical apparatus. Thus the number of atoms in the measured mass of helium produced in unit time became known, and N was calculated to be 6.04×10^{23} .

(b) 1935: In 1910 the American physicist MILLIKAN attempted to determine the charge on a single electron by a very ingenious method. Oil drops of microscopic dimensions electrically charged by the capture of a small number of gaseous ions could be held suspended by a measured electrical field against their natural fall under gravity. The original experiments were vitiated by a number of small errors, which were later corrected. The total electric charge F (termed the *faraday*) on a gram-ion of any singly charged ion, such as Ag^+ or Cl^- , is readily determined by applying Faraday's laws of electrolysis (p. 38), and amounts to 96,500 coulombs. This charge must be equal in magnitude to that of N electrons, or $N = \frac{F}{e}$, whence N is calculated as 6.03×10^{23} .

The three methods quoted are mutually independent, and hence in the practically equal values of N given by them lies the final verification of Avogadro's principle.

Applications of the Avogadro Number.

1. Absolute Atomic Weights.

$$\text{Oxygen: } \frac{16.000}{6.024} \times 10^{-23} = 2.655 \times 10^{-23} \text{ gm.}$$

$$\text{Hydrogen: } \frac{1.0080}{6.024} \times 10^{-23} = 1.673 \times 10^{-24} \text{ gm.}$$

2. Ionic (or Electronic) Charge.

The most accurate estimate is now based on method (b) above, used in reverse. The quantity of electricity required to discharge and deposit one gram-ion of Ag^+ (or of any other singly charged ion) is 96,500 coulombs. Hence the ionic or electronic charge is

$$\frac{96,500}{6.024} \times 10^{-23} = 1.602 \times 10^{-19} \text{ coulombs.}$$

The coulomb, which is the amount of electricity conveyed per second by a current of one ampere, contains almost exactly 3×10^9 electrostatic units (e.s.u.) of electricity, this unit being defined as the charge repelling (in vacuo) an equal charge 1 cm. distant with a force of one dyne. The ionic charge is thus also expressible as

$$1.602 \times 10^{-19} \times 2.9978 \times 10^9 = 4.803 \times 10^{-10} \text{ e.s.u.}$$

3. *The Electronic Mass.*

The behaviour of electrons in electric and magnetic fields depends on the ratio of its charge to its mass, $\frac{e}{m}$, and carefully designed experiments have led to the value 1.759×10^8 coulomb/gm. for this ratio (sometimes called the *specific electronic charge*).

The mass of one electron is therefore

$$\frac{m}{e} \times e = \frac{1.602 \times 10^{-19}}{1.759 \times 10^8} = 9.107 \times 10^{-28} \text{ gm.}$$

4. *G.-formula Weights from X-ray Data.*

From the diffraction of X-rays by crystals of sodium chloride it has been proved that the small unit, or *unit cell*, of which, by continued spatial repetition, the macroscopic crystal is composed, is a cube of side 5.6398 Å. at 18°; and that this cube contains four pairs of ions Na⁺, Cl⁻. Hence the volume at that temperature of one gram-formula weight of sodium chloride is

$$\frac{(5.6398)^3}{4} \times 10^{-24} \times 6.024 \times 10^{23} = 27.015 \text{ c.c.}$$

The density of sodium chloride at 18° is found to be 2.1638 gm./c.c.

The gram.-formula weight is therefore

$$27.015 \times 2.1638 = 58.45(6) \text{ gm.}$$

CHAPTER VI

THE GASEOUS STATE

The Kinetic Theory. Three important facts about gases may be realized from the following considerations:

(i) When 1 c.c. of water at 100°C . 760 mm. is converted into steam at the same temperature and pressure, the volume of the steam is nearly 2 litres.

Therefore *the molecules in steam must be widely separated from one another.*

(ii) If a jar of hydrogen sulphide is opened in a room of ordinary size, only a few seconds elapse before the smell of the gas is perceptible in all parts of the room.

Therefore *the molecules of hydrogen sulphide must be in rapid motion.*

(iii) A gust of wind may blow down an advertisement hoarding.

Therefore *air-molecules in motion exert a pressure.*

These facts, which apply to all gases and not merely to steam, hydrogen sulphide, and air, are the basis of the *kinetic * theory*, which may be expressed more precisely as follows:

At all temperatures above absolute zero (-273°C .), the molecules of a gas are in motion of translation (i.e. they are moving from place to place). They thus possess kinetic energy, and the kinetic energy due to this translatory motion is proportional to the absolute temperature. The real volume of the molecules in a gas at usual temperature and pressure is minute in comparison with the space in which they move and which they therefore *appear* to occupy. Finally, the pressure exerted by a gas on the walls of the vessel containing it is due to the perpetual bombardment of the walls by the molecules of the gas.

It will be useful to refer to some definite figures. In oxygen at N.T.P., the average distance travelled by a molecule between successive collisions is only 0.00001 cm., but this is some 400 times as great as the diameter of the molecule. The average velocity of the molecules is 46,000 cm. per second (i.e. about 15 miles per minute). Hence the number of times *per second* that one oxygen molecule collides with another is, roughly, $\frac{46,000}{0.00001}$ or 4,600,000,000—

* Greek: *kinētikos*, moving.

four thousand six hundred million! Since 1 c.c. at N.T.P. contains 2.7×10^{19} molecules (p. 54), the total number of collisions made by all molecules in 1 c.c. per second is

$$4.6 \times 10^9 \times \frac{2.7 \times 10^{19}}{2} \simeq 6 \times 10^{28}$$

a number expressed as 6 followed by 28 zeros. The factor $\frac{1}{2}$ enters because it takes two molecules to make a collision.

Explanation of the Gas Laws. The kinetic theory affords simple explanations of Boyle's Law, Charles's Law, and other laws concerning the behaviour of gases. The treatment adopted here is not a rigorous one but is intended to illustrate the general argument.

Suppose that n molecules of a gas, each of mass m gm., are enclosed in a cubical vessel with a side of l cm. Suppose further that the molecules are perfectly elastic, so that after impact with a wall of the vessel they have suffered no loss of momentum. The molecules are in random, chaotic motion, but since the pressure on each face of the cube is the same, we may assume that, on the average, a third of the molecules move backwards and forwards from one face to the opposite one, the other two-thirds behaving similarly between the second and third remaining pairs of parallel faces.

Let the average velocity of a molecule be u cm. per second. Then the number of impacts per second it makes on the two faces between which it is moving is $\frac{u}{l}$. Its momentum (i.e. mass \times velocity) when it makes impact is mu , and since it is perfectly elastic it rebounds with a momentum $-mu$ (minus because the direction of movement is now exactly opposite). Hence the *change* of momentum is $mu - (-mu) = 2mu$, and the *rate of change* of momentum is $2mu \times \frac{u}{l}$ per molecule per second. Therefore for all the molecules, at all the faces, the rate of change of momentum is

$$n \times 2mu \times \frac{u}{l} = \frac{2nmu^2}{l}.$$

This gives the total force on the faces; therefore the force per square cm. is $\frac{2nmu^2}{l}$ divided by $6l^2$, or $p = \frac{1}{3} \cdot \frac{nmu^2}{l^3}$

l^3 is, however, the volume of the gas. Let it be v c.c.

$$\text{Then } pv = \frac{1}{3} \cdot nmu^2.$$

- (i) Let two gases be contained at the same pressure in vessels of unit volume. Then $n_1 m_1 u_1^2 = n_2 m_2 u_2^2$. If the temperatures of the two are also equal, then by Avogadro's principle $n_1 = n_2$, and therefore $\frac{1}{2} m_1 u_1^2 = \frac{1}{2} m_2 u_2^2$, i.e. equality of temperature implies equality of average kinetic energy. Since we assume the kinetic energy to vanish at the absolute zero, this equality can be maintained only if absolute temperature is *proportional* to the average kinetic energy.
- (ii) *At constant temperature*, all the factors on the right-hand side of the above equation for pv are constant. Therefore pv is constant. (*Boyle's Law*.)
- (iii) As shown above, $\frac{1}{2} mu^2$ is directly proportional to the absolute temperature, T . Then, for a mole of gas (N molecules),

$$\frac{1}{3} \cdot Nmu^2 = T \times \text{a constant} \\ = RT.$$

$$\therefore pv = RT. \quad (\text{Gas Equation.})$$

- (iv) Keeping p constant in the last equation, it follows that

$$v = kT \\ \text{or } v \text{ varies as } T. \quad (\text{Charles's Law.})$$

- (v) It may also be shown that the average velocity of the molecules of a gas at constant pressure is inversely proportional to the square root of its density.

$$pv = \frac{1}{3} \cdot nm u^2 \\ \therefore u = \sqrt{\frac{3pv}{nm}}.$$

But the density, d , of the gas is equal to $\frac{nm}{v}$.

$$\therefore u = \sqrt{\frac{3p}{d}} = k \sqrt{\frac{1}{d}}. \quad (\text{Graham's Law, p. 61})$$

The Average Velocity of Gaseous Molecules. The average or mean velocity u assumed in sections (i) to (v) above without definition must now be given a more precise meaning. From section (iii) we have, for a mole of gas,

$Nmu^2 = 3RT$, or $\frac{1}{2} Nmu^2 = \frac{3}{2} RT = 819 \text{ calories at } 273^\circ\text{K}$ (see p. 33). The left-hand member of the second equation is the *total kinetic energy* of the N molecules, which is constant at temperature T , in

spite of the fact that the kinetic energy of an individual molecule changes abruptly at every collision it makes. If u_1, u_2, u_3 , etc., are the velocities of individual molecules at any moment, the total kinetic energy is $\frac{1}{2}m(u_1^2 + u_2^2 + u_3^2 + \dots)$, and since this is constant as long as the temperature is unchanged, and m is the same for all molecules, the *sum of the squares of the molecular velocities is constant*, however widely the separate values u_n^2 fluctuate in collisions. The *mean-square-velocity* $\frac{(u_1^2 + u_2^2 + u_3^2 + \dots)}{N}$ is therefore also constant at constant temperature. If we use the symbol $\overline{u^2}$ for the mean-square-velocity, $u = \sqrt{\overline{u^2}}$, the *root-mean-square-velocity*.

Evaluation of the root-mean-square-velocity. From the equation in the preceding section:

$$u^2 = 3 \frac{RT}{Nm} = 3 \frac{RT}{M}.$$

In oxygen at 273° abs.

$$\begin{aligned} u &= \sqrt{3 \frac{RT}{M}} \\ &= \sqrt{(3 \times 8.314 \times 10^7 \times \frac{273}{32})} \\ &= 4.613 \times 10^4 \text{ cm./sec.} \end{aligned}$$

Note that to calculate u in cm./sec. the gas constant R must be taken in c.g.s. units, i.e. ergs per degree (see p. 33).

Again,

$$u^2 = 3 \frac{RT}{M} = 3 \frac{pV}{M} = 3 \frac{p}{\rho},$$

where ρ is the density of the gas in gm./c.c. at the pressure p . If both the pressure and density of a gas at that pressure are known then the temperature of the gas is fixed. For example, the density of oxygen at N.T.P. is 1.428 gm./litre; hence if we say this is the density at 1 atmosphere pressure then we know the temperature must be 273° abs.

$$\begin{aligned} u &= \sqrt{\left(3 \frac{p}{\rho}\right)} \\ &= \sqrt{\left(\frac{3 \times 1.013 \times 10^6}{1.428 \times 10^{-3}}\right)} \\ &= 4.613 \times 10^4 \text{ cm./sec.} \end{aligned}$$

In this method of calculating u in cm./sec. the pressure must be taken, not in atmospheres, but in c.g.s. units as dynes/cm.², and the density must be in gm./c.c. (see again p. 33).

Diffusion. GRAHAM (1833) discovered that a dense gas made its way or *diffused* through a porous partition more slowly than a light one. Quantitative measurement showed that *the rate of diffusion of a gas is inversely proportional to the square root of its density*, a relationship known as *Graham's Law*. The theoretical basis of this law is given above.

If a mixture of gases of different density is enclosed in a porous vessel (e.g. an unglazed 'porous pot'), each will diffuse through the wall at a different rate; hence a partial separation (*atmolysis*) may be effected.

Measurement of rates of diffusion affords a means of determining the molecular weights of gases, but since diffusion is very slow, the related phenomenon of *effusion* is more convenient to employ for this purpose.

Effusion consists in forcing the gas through a minute hole (e.g. small pin-hole). A similar law applies:

$$\text{Rate of effusion varies as } \sqrt{\frac{1}{d}}$$

where d is the density of the gas; no appreciable *atmolysis* can, however, be effected by effusion.

Example: A certain volume of oxygen took 37 minutes to pass through the hole of an effusiometer. Under the same conditions, the same volume of ozone required 45 minutes to effuse. If the molecular weight of oxygen is 32, what is that of ozone?

$$\frac{R \text{ ozone}}{R \text{ oxygen}} = \sqrt{\frac{d \text{ oxygen}}{d \text{ ozone}}}$$

Therefore, since the rates of effusion (R) are inversely proportional to the times taken for equal volumes to effuse,

$$\frac{45}{37} = \sqrt{\frac{d \text{ ozone}}{16}}$$

$$\frac{45^2}{37^2} = \frac{d \text{ ozone}}{16}$$

$$\therefore d \text{ ozone} = 23.7$$

$$\text{and M.W.} = 47.4.$$

Deviations from Boyle's Law. No known gas *accurately* conforms to Boyle's Law, for reasons which are very simple to understand. In the first place, the molecules of a gas exert a force of attraction upon one another, which becomes greater the closer they

are together. The effect of this attraction is to make the volume decrease with rise of pressure more rapidly than it should do according to Boyle's Law.

Secondly, the volume in which molecules are free to move is not quite the volume of the vessel in which they are enclosed, for the molecules themselves have a definite volume. If, for example, the volume of the vessel is V and the actual volume of the molecules is v , then the space in the vessel free from molecules is $V - v$. This factor works in the opposite way to the first, i.e. it makes the volume decrease too slowly with rise of pressure.

Both factors have greater effects at high pressure than at low pressure, since at low pressures (i) the molecules are so far apart that their mutual attraction is negligible, and (ii) the value of v is negligible in comparison with the value of V .

In the modified form of the gas equation $pv = RT$ suggested by VAN DER WAALS, viz.:

$$\left(p + \frac{a}{v^2}\right) (v - b) = RT,$$

the term $\frac{a}{v^2}$ is introduced to correct the discrepancy due to the force of attraction between the molecules, and the term b to correct for the actual volume of the molecules. It gives results in good, but not complete, agreement with experimental data. The constants a and b are small, and specific for every gas.

The volume b , from which molecular motion is excluded, is not the same as v , the total volume of n molecules in the gas, as might at first be thought. If round the centre of a molecule x (regarded as spherical) of radius r and volume $\frac{v}{n}$ a sphere of radius $2r$ is constructed, another molecule achieves its closest approach to x when its centre lies in the surface of this sphere, of volume $\frac{8v}{n}$. Since this is the 'excluded' volume per pair of molecules, the total, b , for all n molecules is $4v$.

Liquefaction of Gases. In 1798, MARTIN VAN MARUM (1750-1838)—the discoverer of ozone—described the liquefaction of ammonia, which he effected by means of increased pressure. NORTHMORE in 1806 liquefied chlorine in the same way, while in 1823 FARADAY succeeded in liquefying sulphur dioxide, carbon dioxide, nitrous oxide, cyanogen, and hydrogen chloride.

Gases may also be liquefied by the application of low temperatures—sulphur dioxide, for instance, liquefies at atmospheric pressure if passed into a U-tube surrounded by a freezing-mixture of ice and salt—and by 1865 practically all the known gases except hydrogen,

oxygen, nitrogen, carbon monoxide, methane, and nitric oxide had been obtained in the liquid state. The six stubborn ones were called 'permanent gases,' for even when subjected to enormous pressures they showed no signs of liquefying. Faraday was equally stubborn; he refused to believe in their permanency, though he found the term useful at the time.

A better understanding of the principles involved in the liquefaction of gases resulted from the classical researches of ANDREWS (1869) on carbon dioxide. Andrews measured the volume occupied by a given mass of carbon dioxide at different pressures but at a constant temperature, and plotted the results as a curve. Since the measurements were all taken at the same temperature the curve is known as an *isothermal*. He then repeated the process for various different temperatures, so obtaining a series of isothermals. These curves are given in Fig. 23.

The isothermal for 48.1° shows that the volume of the gas at this temperature decreases regularly with rise of pressure. In isothermal 13.1° , however, starting from the right, there is a small portion over which the change in volume is regular, but a sharp break soon occurs and the volume suddenly decreases by a large amount. Further increase in pressure has very little effect. The explanation is that, at the break, the gas condenses to a liquid,

the volume of which is small compared with that of the gas. The steep portion of the isothermal on the left represents the effect of increased pressure upon the almost incompressible liquid.

The isothermals at 21.5° and 31.1° are similar, though the points at which liquefaction occurs are different, and higher pressures are required to cause it. Above 31.1° , the curve shows *no* horizontal portion at all, indicating that no liquefaction has taken place.

When Andrews warmed a tube containing both liquid and gaseous carbon dioxide, he observed that, at 31.1° , the boundary between the two flickered and disappeared, though the liquid did not boil. At this temperature, in fact, the density of liquid carbon dioxide and that of gaseous carbon dioxide become the same, so that no distinction between

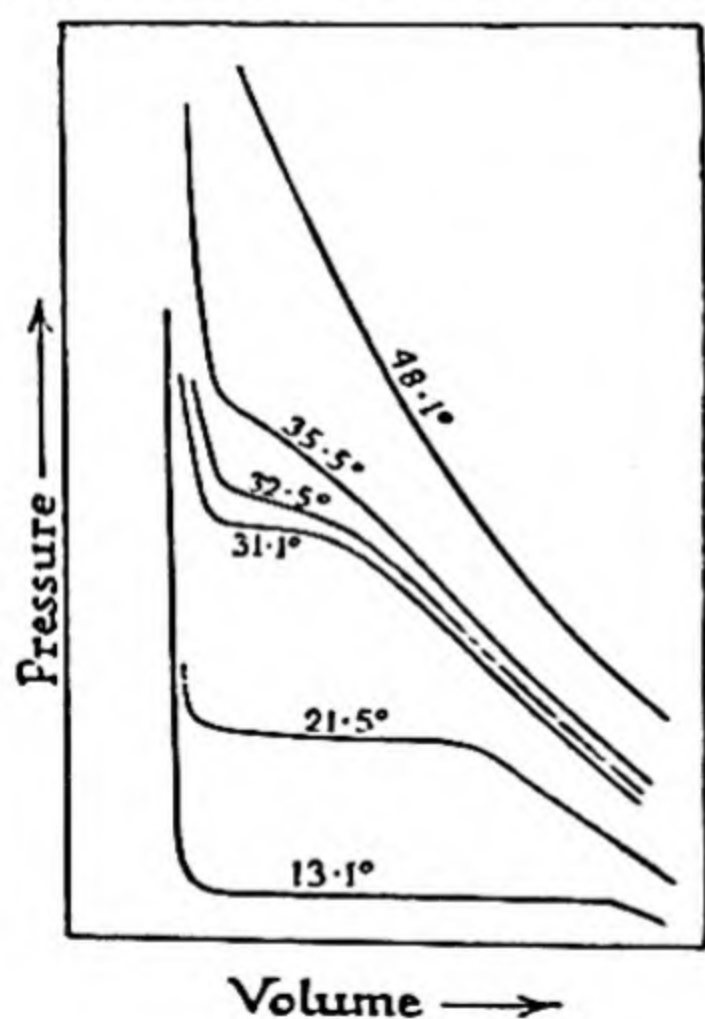


FIG. 23.
ISOTHERMAL CURVES FOR
CARBON DIOXIDE (ANDREWS)

carbon dioxide become the same, so that no distinction between

the two forms any longer exists. To put the same thing another way, 31.1° is the temperature at which the molecules of liquid carbon dioxide become so far apart from one another that the substance loses its liquid characteristics and is indistinguishable from the substance obtained by compressing gaseous carbon dioxide to the same density at this temperature.

Andrews called 31.1° the *critical temperature* of carbon dioxide, and the pressure (72.9 atmospheres) at which the distinction between the gas and liquid disappeared at this temperature, the *critical pressure*. The reciprocal of the density of the substance at the critical point he called the *critical volume*.

Further work has shown that every gas has its own critical temperature, above which no pressure, however great, can make it assume the liquid form. The critical temperatures of some common gases are given below (compare with molecular volumes, p. 32):

Ammonia 132.5°	Hydrogen -240°
Carbon dioxide 31°	Helium -268°
Sulphur dioxide 157°	Nitrogen -147°
Nitrous oxide 36.5°	Oxygen -119°
Chlorine 144°	Methane -82°
Nitric Oxide -96°	

It will be clear from this table that the reason for the lack of success attending early attempts to liquefy the so-called 'permanent' gases was undue reliance upon great pressure alone, and failure to cool the gases sufficiently. Andrews's work showed that the essential condition for the liquefaction of a gas is to cool it below its critical temperature.

As soon as this was realized, further progress became possible. The chief difficulty was to find means of cooling gases sufficiently, for even a freezing-mixture of solid carbon dioxide and ether gives only so comparatively high a temperature as -90° . A solution of the problem came from a quite unexpected source. CAILLETET, a French engineer, was carrying out upon acetylene experiments similar to those of Andrews upon carbon dioxide, using a powerful hydraulic press to obtain the necessary high pressures. One day a valve was accidentally left open, and the compressed gas suddenly expanded. In the tube, however, a thick mist of liquid droplets appeared, and Cailletet realized that these were droplets of liquid acetylene. Expansion of a compressed gas under adiabatic conditions—that is, under conditions in which no transference of heat occurs between the gas and its surroundings—does in fact cause the temperature of the gas to fall. In expanding against the pressure the gas has to do work, and obtains the necessary energy

from the kinetic energy of its molecules. But since the temperature of a gas is a measure of its kinetic energy, decrease in the latter implies a fall in temperature.

A somewhat similar phenomenon was observed in 1862 by JOULE and THOMSON (later LORD KELVIN), who found that if a highly compressed gas is allowed to escape through a minute aperture into a region of much lower pressure, it becomes cooler. This is because, on expanding, it has to overcome the mutual attraction between its molecules. Here again it obtains the energy necessary for this purpose from the kinetic energy of the molecules themselves, and a fall in temperature occurs.

Cailletet repeated his adiabatic experiment with oxygen cooled in liquid sulphur dioxide, and obtained a mist of the liquefied gas (2nd December 1877 *), but the controlled use of the Joule-Thomson effect was first successfully applied by the German scientist LINDE in 1895.

LINDE compressed air to 65 atmospheres and allowed it to expand through a spindle valve. The cooler air so produced was circulated over the pipe conveying the compressed air to the valve, so that the cooling effect was continuous and the temperature steadily fell. Finally, part of the air liquefied. When he judged that sufficient had been collected, Linde opened the tap of the receiver and 'allowed the beautiful bluish liquid to gush out into a large bucket.'

Modern liquefiers, of which further details are given on p. 488, work on this principle. To liquefy hydrogen and helium, however, the gases must first be cooled in another way, since at ordinary temperatures they show a *positive* Joule-Thomson effect, i.e. they become hotter when passed through the valve. When the temperature is low enough (e.g. -90° for hydrogen at a compression of 100 atmospheres) they behave normally. In order to obtain these low initial temperatures, the gas is passed through tubes surrounded by rapidly boiling liquid air. Liquid air boils at about -190° , but if it is made to boil rapidly, by reducing the external pressure, its temperature—like that of any other liquid boiling under similar conditions—falls, since the heat necessary for vaporizing some of the liquid is taken from the rest.

Liquid hydrogen was first obtained, as a mist which evaporated almost instantaneously, by OLSZEWSKI in 1895. He used Cailletet's original method of sudden expansion, previously cooling the hydrogen in solid nitrogen subliming rapidly under low pressure. The first to prepare liquid hydrogen in bulk was SIR JAMES DEWAR

* The Swiss physicist PICTET also obtained liquid oxygen in the same month. He allowed compressed oxygen, cooled in solid carbon dioxide, to escape from a valve, and obtained a jet of the liquid—which, however, evaporated before he could collect it.

(1842-1923), who in 1898 employed the Joule-Thomson effect with hydrogen previously cooled to the necessary temperature. Helium, the most difficult of all gases to condense to a liquid, was liquefied (B.P. -268.7°)—and solidified (M.P. -272°)—by KAMERLINGH ONNES of Leiden in July 1908. He too used the Joule-Thomson effect, cooling the helium beforehand in solid hydrogen (-259°).

Temperatures only a small portion of a degree (0.0044°) above absolute zero have been obtained by cooling certain salts, e.g. chrome alum (p. 573), in liquid helium and subjecting them to a powerful magnetic field. On switching off the field, the temperature of the salt falls to the astonishingly low values indicated.

CHAPTER VII

CHEMICAL ENERGY (I):

THERMOCHEMISTRY

Historical. In 1780, LAVOISIER and LAPLACE stated that if heat is *absorbed* when chemical reactants unite, then the same amount of heat is *liberated* when the product is reconverted into the original substances; and, conversely, that if heat is evolved during the formation of a compound, the same amount of heat is absorbed in the decomposition of the compound into the substances from which it was formed. They brought forward experimental evidence in support of the statement, and may thus be said to have established that particular branch of chemistry known as **Thermochemistry**.^{*} Other notable workers on thermochemistry were G. H. HESS (1802-50), J. THOMSEN (1826-1909), E. H. SAINTE-CLAIRE DEVILLE (1818-81), J. H. VAN'T HOFF (1852-1911), and M. P. E. BERTHELOT (1827-1907).

Exothermic and Endothermic Reactions. In the majority of chemical reactions heat is liberated, and such reactions are consequently described as exothermic.[†] When carbon is burned to carbon dioxide, for instance, much heat is evolved, and the combustion of carbon or carbon compounds is the commonest method employed by man for obtaining a supply of heat energy. *Endothermic* [‡] reactions, which involve an absorption of heat, are much less numerous, though by no means rare. Familiar examples are the combination of carbon with sulphur to form carbon disulphide, and the synthesis of nitric oxide from nitrogen and oxygen at high temperatures.

Energy Units in Thermochemistry. Until recently all chemical heat changes were expressed in calories, a calorie being defined as the amount of heat required to raise the temperature of one gram of water from 15° to 16° C.§ The calorie (*cal.*) is a rather small unit, and the kilogram-calorie (*kcal.*), i.e. 1,000 calories, is often more convenient to use. The calorie is, however, an arbitrary unit of energy, outside the c.g.s. system, in which the unit of energy is the

^{*} Greek, *thermē*, heat.

[†] Greek, *exō*, outside.

[‡] Greek, *endon*, within.

[§] The specific heat of water is not constant, but varies slightly at different temperatures. Hence in fixing the value of the calorie, a particular one-degree range had to be selected.

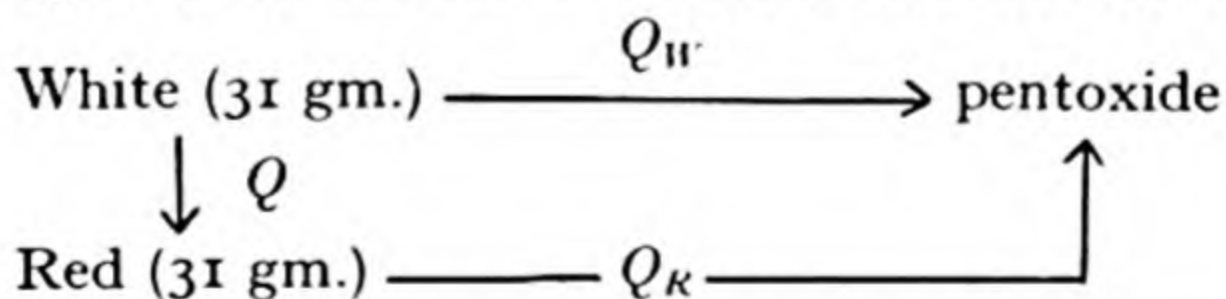
erg. It is now increasingly preferred to express all chemical energy changes in terms of the *joule*, which is defined as 10^7 ergs: a *kilo-joule* (symbol *kJ*) is 10^3 joules. The *mechanical equivalent of heat* (or the *Joule equivalent*) is 4.186 joule/cal. (see p. 96 for the relation of the atomic energy unit, the *electron-volt*, to the calorie).

Hess's Law. It was shown by HESS in 1840 that the *total* heat evolved or absorbed in a chemical reaction is independent of the intermediate stages (if any) by which the reaction proceeds, and depends solely upon the nature and quantity of the reactants and products. Today we see the law as a necessary corollary of the law of the conservation of energy, but in Hess's time the position was reversed, for he advanced his law, based on thermochemical experiments, in support of the more fundamental generalization.

Factors Affecting Chemical Heat Changes. The magnitude of the heat change in a given reaction depends on a number of factors, of which the most important is *the physical state of the reactants and products*. When a gram-molecule of hydrogen (2.016 gm.) is burnt in oxygen 57.8 kcal. are released when the product is *steam*, but 68.3 kcal. when it is *water*. Three distinct forms of elementary phosphorus are known respectively as white, red, and black phosphorus (p. 462). When 31 gm., or 1 gram-atom, of phosphorus in each of these varieties are burnt in oxygen to yield in each case equal weights of phosphorus pentoxide in the same solid form, the following quantities of heat Q are liberated:

Phosphorus	Q (kcal.)
White	180.0
Red	175.6
Black	169.7

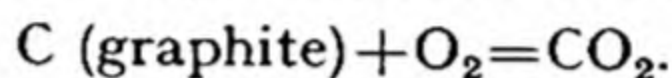
From Hess's law we can deduce that the heat released Q_W must be unaltered if before burning white phosphorus we convert it into an equal weight of the red form and then burn the latter:



Hence $Q_W = Q + Q_R$, whence $Q = 4.4 \text{ kcal.}$ It follows that the conversion of 31 gm. of white into red phosphorus is accompanied by a release of 4.4 kcal. of heat.

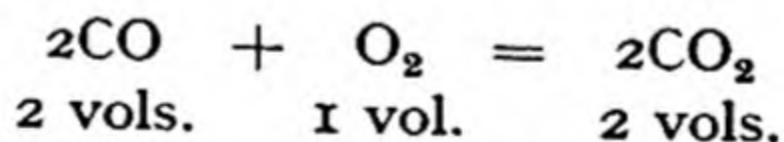
Other factors influencing chemical heat change are (1) the temperature at which reaction is conducted, (2) whether, especially in cases involving gases, reaction proceeds at *constant volume* (with change of pressure), or at *constant pressure* (with change of volume).

Heat Changes at Constant Volume or Constant Pressure. For the purposes of argument let us suppose that we have at our disposal a calorimeter with a stout-walled reaction chamber closed by a gas-tight piston. We charge it with a weighed amount of graphite, and a considerably greater volume of pure oxygen (at atmospheric pressure) than is needed to burn the carbon to carbon dioxide. The piston, weighted to exert 1 atmospheric pressure on the contents of the calorimeter, is locked in position and the carbon fired:



The heat Q_V registered by the calorimeter is clearly the heat of the combustion of the graphite conducted at *constant volume*. If, when the temperature of the calorimeter and its contents has returned to normal, the piston, with unchanged weighting, is released, it must slightly descend through a volume equal to that of the original graphite. The work of compression thus done on the gaseous contents is transferred as its equivalent of heat to the calorimeter. The total heat released, Q_P , is the heat of combustion at *constant pressure* (1 atmosphere). Although small the difference between Q_V and Q_P is definite.

Suppose now in the same calorimeter under similar conditions a mixture of 2 volumes of carbon monoxide with 1 volume of oxygen, introduced at 1 atmosphere pressure, is fired. The explosive reaction, $2\text{CO} + \text{O}_2 = 2\text{CO}_2$, follows, and heat, Q_V , is first released, but on unlocking the piston as before it descends (under 1 atmosphere pressure) until the volume of contained gas is $\frac{2}{3}$ of that originally present:



The difference between Q_V and Q_P in this experiment will be more considerable and is easily estimated. Hess's law enables us to substitute for the actual explosive combination an imaginary slow action, during which the piston, always under 1 atmosphere pressure, falls continually and gradually. The volume through which it falls in the compression is the volume of the x gram-molecule of oxygen in the unfired mixture (see previous equation). Hence the work done on compression is $P \cdot xV$, where V is the G.M.V. of oxygen at 1 atmosphere and temperature T . But

$$\begin{aligned} x(PV) &= x(RT) \\ &= x \cdot 596 \text{ cal. at } 25^\circ. \end{aligned}$$

Energy and Enthalpy. Since by the law of Hess the heat change in a chemical reaction does not depend on the intermediate stages, i.e. on the *path* of the reaction, it can only depend, if the reaction is

conducted at constant *volume*, on the difference between the energy U_2 of the products and the energy U_1 of the reactants:

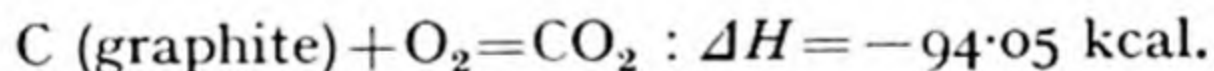
$$Q_V = U_2 - U_1 = \Delta U.$$

But if the reaction proceeds at constant *pressure* P :

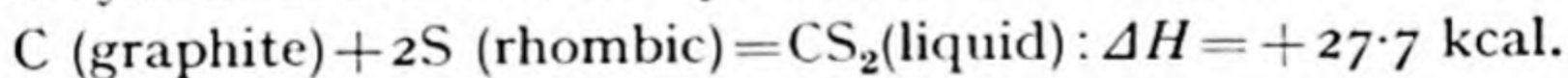
$$\begin{aligned} Q_P &= (U_2 - U_1) + P(V_2 - V_1) \\ &= (U_2 + PV_2) - (U_1 + PV_1) \\ &= H_2 - H_1 = \Delta H. \end{aligned}$$

In the examples of the previous paragraph U_1 is the energy of graphite and oxygen, or of carbon monoxide and oxygen before combustion, and U_2 the energy of the resulting carbon dioxide. The quantity H , defined analytically as $U + PV$, is commonly termed *heat content*, but this term has not been everywhere regarded as appropriate. Translation into *enthalpy** has the advantage that the Greek word may, like 'oxygen,' be used as a mere label. It is today the universal practice to express chemical heat changes as changes of enthalpy, ΔH , i.e. as related to reaction occurring at *constant pressure*. When reactants are brought to a given temperature T before reaction, and products to the same temperature at its close, then Hess's law enables us to disregard temperature changes during reaction, and state that the heat of reaction is that of one occurring at the constant temperature T . By common agreement the standard condition of pressure is *1 atmosphere*, and the standard temperature 25°C .

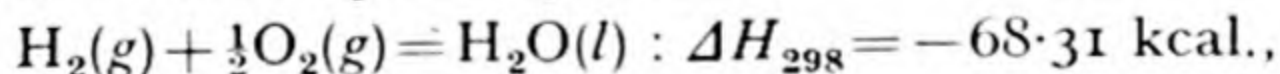
The Sign of Thermochemical Quantities. It should be carefully noted that heat *released* during a chemical reaction (exothermic reaction) implies a *decrease* of the enthalpy of the chemical system (H_1 greater than H_2), and is in consequence reckoned *negative*; for example:



Conversely, an endothermic reaction implies an *increase* of enthalpy of the system and is reckoned *positive*; for example:



Thermochemical Equations. Previous paragraphs will have emphasized that a thermochemical equation is of little value unless it is precise. The complete equation,

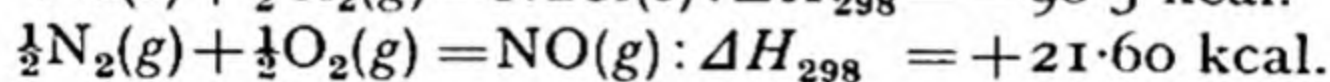
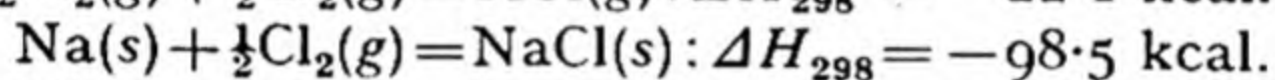
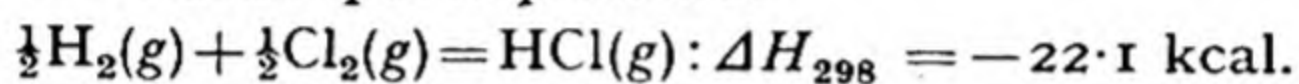


may be expanded as follows. When one G.M.W. (2.016 gm.) of gaseous molecular hydrogen at 1 atmosphere pressure reacts at 25° (298° abs.) with $\frac{1}{2}$ G.M.W. (16.0 gm.) of gaseous molecular oxygen at the same pressure to give one G.M.W. (18.016 gm.) of

* Greek *thalpō*, to heat.

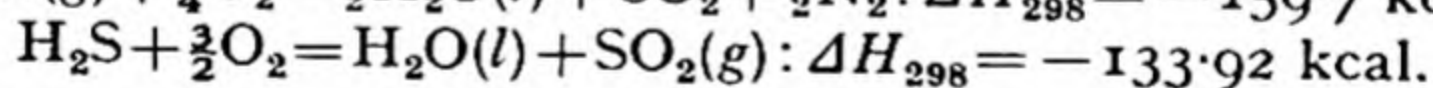
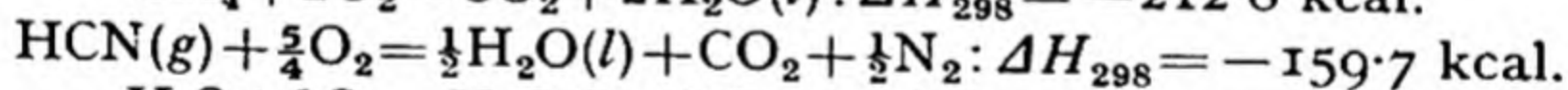
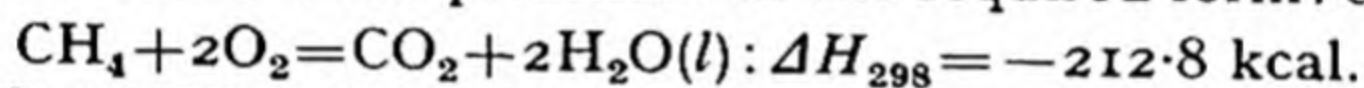
water at 25°, the heat liberated is 68.31 kcal. It should be noted that the expressions $\frac{1}{2}\text{O}_2$ and O have extremely different meanings: the latter implies one gram-atom (16 gm.) of *atomic* oxygen. Where no ambiguity can reasonably arise, the qualification (g) is often omitted, but it is still to be understood that gases are at 1 atmosphere pressure. For solids the added qualification (s) means that form normal at 25°;—C(s) is graphite, P(s) is 'white' phosphorus, and S(s) 'rhombic' sulphur.

Heat of Formation. The heat of formation of a compound is the change of enthalpy (heat content) when one molar weight, or one gram-formula weight, of the compound is formed at 25° C. from its elements in their pure forms normal at this temperature, all gases being under 1 atmosphere pressure.



Heat of Combustion. The heat of combustion of a compound is the change of enthalpy (heat content) when one molar weight, or one gram-formula weight, of the compound is completely burned at 25° C. in oxygen at 1 atmosphere pressure.

(The combustion cannot be conducted at 25°, nor usually in oxygen at 1 atmosphere pressure, but application of Hess's law enables the results to be presented in the required form: see p. 70.)



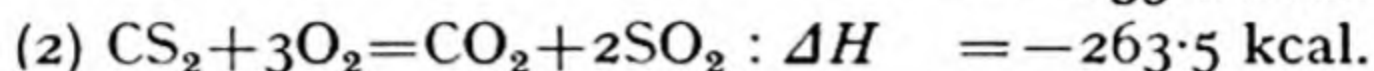
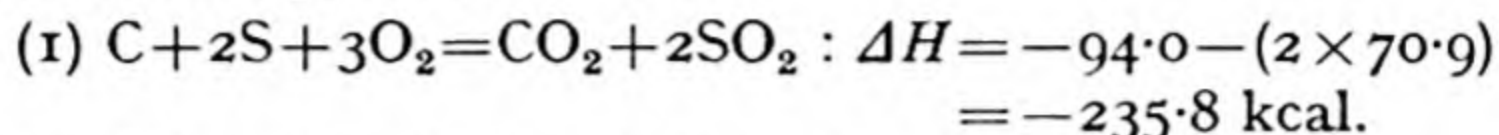
Heat of Reaction. The heat of reaction is the change of enthalpy (heat content) in a reaction conducted at 25° C. between compounds in gram-molecular or gram-formula weight quantities, all gases being at 1 atmosphere pressure, and other compounds in their normal forms at that temperature.

Heat of reaction is formally related to the heats of formation of the compounds taking part in the reaction, as shown in the following example:

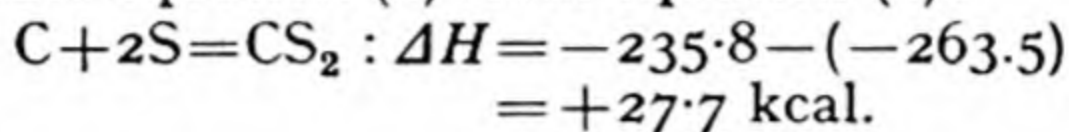
	$\text{NO}_2(g)$	+	SO_2	=	NO	+	$\text{SO}_3(g)$	
Heats of formation (kcal.)	8.1		-70.9		21.6		-94.4	
Totals on each side			-62.8				-72.8	
Heat of reaction					62.8 - 72.8			= -10.0 kcal.

Thermochemical Calculations. The law of Hess permits the manipulation of thermochemical equations by addition and subtraction in the same way as algebraic equations may be treated.

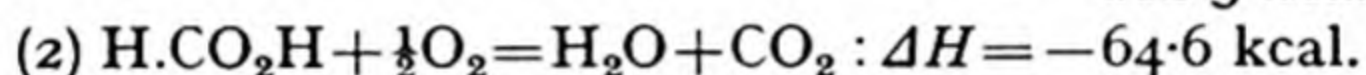
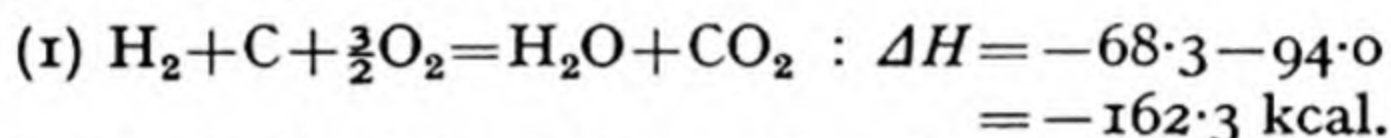
Examples: (i) The heats of formation of sulphur dioxide, SO_2 , and carbon dioxide, CO_2 , are respectively -70.9 kcal. and -94.0 kcal. The heat of combustion of carbon disulphide, CS_2 , is -263.5 kcal. Calculate the heat of formation of carbon disulphide:



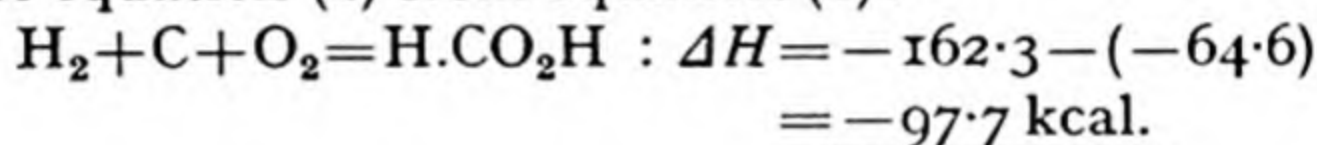
Subtract equation (2) from equation (1):



(ii) The heats of formation of water and carbon dioxide are respectively -68.3 kcal. and -94.0 kcal. The heat of combustion of formic acid, $\text{H.CO}_2\text{H}$, is -64.6 kcal. Find the heat of formation of the acid:

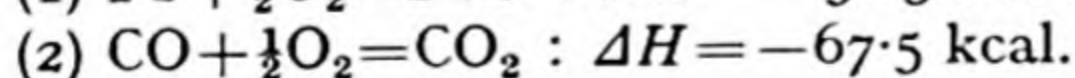
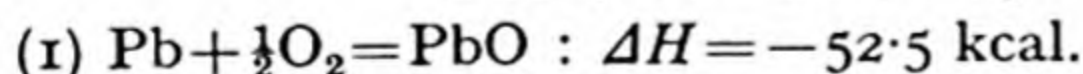
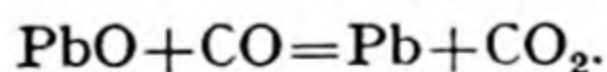


Subtract equation (2) from equation (1):

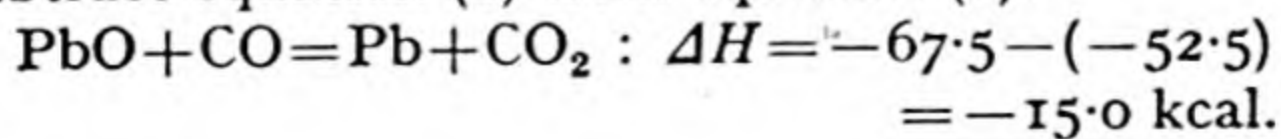


Although the combination of carbon and sulphur is endothermic, carbon disulphide is obtained by passing sulphur vapour over red-hot carbon (p. 405), but the process cannot be carried out directly in a calorimeter. Formic acid cannot be prepared directly from its elements by any known reaction. Nevertheless Hess's law enables us to calculate the heat which would be released in such a reaction. The heats of formation of most organic compounds are obtained through their heats of combustion as in Example (ii).

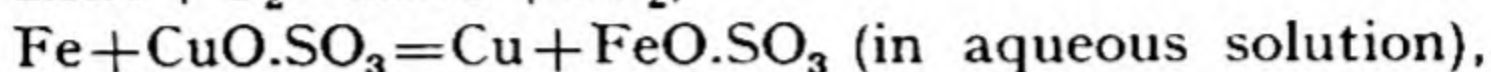
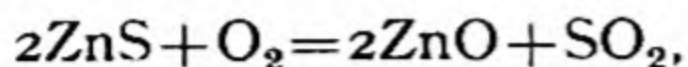
(iii) The heat of formation of lead monoxide, PbO , is -52.5 kcal. and the heat of combustion of carbon monoxide, CO , is -67.5 kcal. Find the heat of the reaction:



Subtract equation (1) from equation (2):

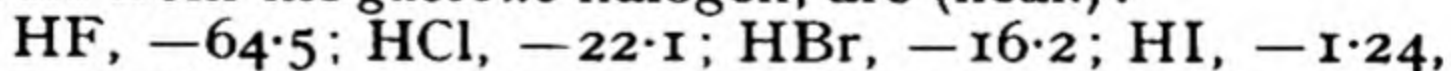


Significance of Chemical Heat Changes. It was the view of the chemists of the late eighteenth century that the spontaneous union of two elements was caused by their 'affinity' for each other. Much effort was expended in attempts to compare 'affinities' by means of displacement reactions. For example, from the reactions:



it was concluded that zinc had a greater affinity for oxygen than for sulphur: and that iron had a higher affinity for oxygen than copper. Although this attitude greatly advanced the progress of chemistry by stimulating the search for appropriate reactions, numerous apparent contradictions emerged: but the inquiry was frustrated principally because no numerical value could be assigned to the property of affinity.

From the later development of quantitative thermochemistry it appeared that at last this difficulty might be surmounted. It was proposed, and advocated especially by French chemists under the leadership of BERTHELOT, that the heat of formation of a compound is a true measure of the mutual affinity of its constituent elements: and further that a measure of the so-called 'driving force' of chemical reactions could be seen in the amount of energy liberated as heat. It does indeed seem at least plausible that the stability of a compound should be measurable by the energy dissipated in its formation. Consultation of a modern table of heats of formation and reaction verifies that the idea is widely supported. To give only two instances: the heats of formation of the hydrogen halides, in each case from the *gaseous* halogen, are (kcal.):



and give a satisfactory comparison of their relative stability, for example to oxidation: hydrogen fluoride cannot by purely chemical means be oxidized to fluorine (p. 539), while the iodide is so readily oxidized that it is one of the most powerful reducing agents. The heats of formation of metallic oxides, e.g. (in kcal.)

$\text{CaO}, -151.3; \text{ZnO}, -83.2; \text{FeO}, -63.7; \text{CuO}, -37.1; \text{HgO}, -21.7,$ are in good agreement with the readiness with which the oxides can be reduced to metal.

The existence of spontaneous but *endothermic* reactions, and of *reversible* reactions, implies, not that these ideas about heat of formation are necessarily untrue, but that they are incomplete. There must be other factors concerned in causing chemical reactions, which will be discussed later (Chapter XI).

CHAPTER VIII

CLASSIFICATION OF THE ELEMENTS

When you can measure what you are speaking about and express it in numbers, you know something about it.

LORD KELVIN.

NO CLASSIFICATION of the elements not founded upon properties of their atoms expressible uniquely as numbers can hope to win permanent acceptance. Arrangements upon other, qualitative, bases must always be vulnerable to the influence of opinion, or even of fashion. Moreover, the properties chosen as criteria should be exempt from the effect of change of physical conditions, such as pressure or temperature: and they must not depend upon the aggregation of atoms in the physical forms of elements. In short the desirable properties must be those of the atoms in isolation. Thus, for example, melting points, boiling points, density, or electrical conductivity, although expressible in numbers, and of great interest once a classification has been settled, would not be suitable properties on which to base it.

Cannizzaro, in 1860, triumphantly secured the belated acceptance by his contemporaries of Avogadro's principle, and by demonstrating how it could be applied to fix atomic weights uniquely (p. 45) brought order into a sphere of chemistry that had never before been subject to a generally accepted guiding principle. From its earliest announcement by FRANKLAND (1825-99) in 1852 the doctrine of chemical *valency* gained ground, and KEKULÉ in 1864 laid down the practical method for the determination of this atomic property as follows:

(a) Let it be proved that an element A combines with another, B, to give a stable compound of molecular formula, AB_n .

(b) Let it be further proved that the combining power of B is indivisible (or unitary).

(c) Then in the compound AB_n the combining power of A must be sub-divided into n parts, and n is the valency of A.

Section (a) requires a determination not only of the molecular weight of AB_n but also a knowledge of the atomic weights of A and B; to these demands Avogadro's principle gave the complete answer. In regard to section (b) no complete proof could be given, but it was

assumed that the combining powers of the halogens, as well as that of hydrogen, were indivisible: in short these elements were *univalent*. Kekulé fully realized that to determine the valency of A uniquely attention should be confined to compounds containing within their molecules only *one* of its atoms, and that elements more than univalent, such as oxygen, should be used with caution as the test-element B.

The Periodic Classification. At the time, about 1870, of the first promulgation of a convincing system of classification, its chief founder, MENDELÉEFF (1834–1907), naturally adopted as his basis the two then available numerical atomic properties of weight and valency. The essence of his system is that when the elements are written in ascending order of atomic weight, *elements of equal valency recur at fixed intervals*. Such a recurrence implies a *periodicity** in such general chemical properties as arise from equality of valency. If we fix our attention on the univalent alkali-metals as markers, the whole series of atoms can be divided into successive *periods*, each beginning with such a metal. Today the inert elements, helium (He) neon (Ne), argon (Ar), krypton (Kr), and xenon (Xe), with zero valency, might be thought more suitable as marker elements to delimit the periods, but the discovery of these gases was not to begin until twenty-five years later. It is significant that, excepting helium, each of these inert elements fitted into the atomic series between a halogen and an alkali-metal: that is between *electronegative* elements, whose atoms tend strongly to take up an electron and give a negative ion, e.g. Cl^- , and *electropositive* elements, whose atoms tend no less strongly to release an electron and become positive ions, e.g. Na^+ .

The English chemist NEWLANDS (1837–98) had in 1865 proposed a general ‘law of octaves,’ asserting that in the series of elements arranged in order of increasing atomic weight similar chemical properties recur after an interval of seven or of a multiple of seven elements. This principle proved to be an over-simplification. Unlike his predecessor, Mendeléeff asserted his conviction of the rightness of his system by venturing to correct the atomic weights of elements whose apparent valencies were misplaced in the system of recurrence; and by leaving unoccupied places for undiscovered elements. ‘I will describe,’ he wrote, ‘the properties of some elements whose discovery is to be expected, in order to help the attainment of a new proof of the justice of the periodic law, a proof which is very definite, although it will be realized only in the future.’

* A *periodic* phenomenon is one that is repeated at intervals, e.g. the appearance of *Punch* on Wednesdays. Successive repetitions of the phenomenon need not be *exactly* similar, but show at least a general similarity.

MENDELÉEFF'S SECOND TABLE (1871)

Series	Group I — R ₂ O	Group II — RO	Group III — R ₂ O ₃	Group IV RH ₄ RO ₂	Group V RH ₃ R ₂ O ₅	Group VI RH ₂ RO ₃	Group VII RH R ₂ O ₇	Group VIII — RO ₄
1 2	H=1 Li=7	Be=9.4	B=11	C=12	N=14	O=16	F=19	
3 4	Na=23 K=39	Mg=24 Ca=40	Al=27.3 —=44	Si=28 Ti=48	P=31 V=51	S=32 Cr=52	Cl=35.5 Mn=55	Fe=56, Co=59 Ni=59, Cu=63
5 6	(Cu=63) Rb=85	Zn=65 Sr=87	—=68 ?Yt=88	—=72 Zr=90	As=75 Nb=94	Se=78 Mo=96	Br=80 —=100	Ru=104, Rh=104 Pd=106, Ag=108
7 8	(Ag=108) Cs=133	Cd=112 Ba=137	In=113 ?Di=138	Sn=118 ?Ce=140	Sb=122 —	Te=125? —	I=127 —	— — — —
9 10	(—) —	— —	— ?Er=178	— ?La=180	— Ta=182	— W=184	— —	Os=195, Ir=197 Pt=198, Au=199
11 12	(Au=199) —	Hg=200 —	Tl=204 —	Pb=207 Th=231	Bi=208 —	— U=240	— —	— — — —

Reference to his second table will show that he left gaps under boron, aluminium, and silicon, since not to have done so would have thrown succeeding elements out of the positions which their chemical nature plainly required them to fill. These three gaps, he argued, represent the spaces for three hitherto undiscovered elements, which he proposed to call provisionally *eka-boron* (Sanskrit, *eka*, one), *eka-aluminium*, and *eka-silicon* respectively.

Then, since *eka-boron* falls between calcium (A.W. 40) and titanium (A.W. 48), he predicted that its atomic weight would be 44; and by comparisons and considerations of this kind he was able to make very precise forecasts about the three elements and their compounds. In less than twenty years, all were discovered. *Eka-boron* is *scandium* (NILSON, 1879), *eka-aluminium* is *gallium* (DE BOISBAUDRAN, 1875), and *eka-silicon* is *germanium* (WINKLER, 1886). The table below illustrates the detailed success of Mendeléeff's prophecy. The same kind of agreement was found in the other two cases.

Instances in which atomic weights were settled by reference to the table include that of uranium, which was believed to have an atomic weight of 119. There was, however, no space in the table for an element of this atomic weight, possessing the properties of uranium.

<i>Predicted for Eka-silicon, 'E'</i>	<i>Experimentally determined for Germanium, Ge</i>
Atomic weight 72 Specific gravity 5.5 Chloride, ECl_4 , liquid boiling slightly below 100° , S.G. 1.9 Compound $\text{E}(\text{C}_2\text{H}_5)_4$, liquid, boiling at 160° , S.G. 0.96	A.W. 72.60 S.G. 5.47 Chloride, GeCl_4 , liquid B.P. 86° , S.G. 1.9 Compound $\text{Ge}(\text{C}_2\text{H}_5)_4$, liquid, boiling at 163.5° S.G. rather less than 1

On the other hand, if the atomic weight of uranium were not 119, but 238, the element would find an appropriate niche at the bottom of Group VI. Further experiment showed that the true value was 238.

A second instance is provided by indium, which according to WINKLER had an equivalent of 38 and was believed to have an atomic weight of 76. Mendeléeff, however, maintained that since there was no gap between arsenic (75) and selenium (78), the atomic weight of indium could not be 76, but must be some other multiple of 38, or 38 itself. On the last assumption the metal would be univalent, and its place would be that already occupied

by potassium (39); hence the atomic weight could not be 38. But, 'assuming the oxide to be In_2O_3 , the atomic weight equals 38×3 , or 114, and the element goes into the third group, in which there is in fact between $\text{Cd} = 112$ and $\text{Sn} = 118$ a vacant place for an element with an atomic weight of about 114.' Mendeléeff confirmed this view by redetermining the specific heat of indium, which he found to be 0.055. According to Dulong and Petit's Law, the atomic weight of indium should therefore be roughly $\frac{6.4}{0.055}$, that is 116.

Since Mendeléeff's time only three, apparently intractable, cases of misplaced order in the system have survived:

(i) Argon (39.94), although obviously to be placed in Group O with the other inert elements, has a greater atomic weight than potassium (39.10).

(ii) Tellurium (127.61), although a very close analogue of sulphur and selenium in Group VI, appears to succeed iodine (126.91) in Group VII.

(iii) Nickel (58.71) and cobalt (58.94) are very similar in properties, but in the sequence iron, cobalt, nickel, copper both iron and cobalt have numerous compounds in which the metals are both trivalent, while in the compounds of nickel and copper bivalency is far more prominent.

These exceptions to the expected order have received a full explanation in recent years in the discovery of isotopes (p. 98).

Atomic Number. Both Newlands and Mendeléeff used the term *atomic number* as meaning the ordinal number of an element in the atomic weight series, and the latter, in the anomalous cases (ii) and (iii) mentioned above, was, without realizing the implication, elevating atomic number to a greater significance than atomic weight. On p. 49 some examples were given showing that the wave-length of X-radiation emitted from a given target suffering the electronic bombardment is inversely related to its atomic weight. In 1913 the physicist MOSELEY (1887-1915) explored this relation for a large range of solid materials as targets, determining the wave-lengths of the radiation with a Bragg X-ray spectrometer (Fig. 22). His task was simplified by the fact that the wave-lengths emitted by elements are independent of their states of chemical combination. It was found that the *frequency*, which is proportional to the reciprocal of the wave-length, increased regularly with atomic number (Z), and in particular that while a plot of $\sqrt{\text{frequency}}$ against atomic weight was irregular in detail a plot against Z gave an accurately straight line, showing equal steps for an increase of Z by unity.

THE PERIODIC TABLE (International Atomic Weights, 1957)

Period	Group O	Group I A B	Group II A B	Group III A B	Group IV A B	Group V A B	Group VI A B	Group VII A B	Group VIII
1		1 H 1.0080							
2	2 He 4.003	3 Li 6.940	4 Be 9.013	5 B 10.82	6 C 12.011	7 N 14.008	8 O 16.0000	9 F 19.00	
3	10 Ne 20.183	11 Na 22.991	12 Mg 24.32	13 Al 26.98	14 Si 28.09	15 P 30.975	16 S 32.066	17 Cl 35.457	
4	18 Ar 39.944	19 K 39.100	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.95	24 Cr 52.01	25 Mn 54.94	26 Fe 55.85 27 Co 58.94 28 Ni 58.71
5	36 Kr 83.80	37 Rb 85.48	38 Sr 87.63	39 Y 88.92	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc (99)	44 Ru 101.1 45 Rh 102.91 46 Pd 106.4
6	54 Xe 131.30	55 Cs 132.91	56 Ba 137.36	57 La—71 Lu 138.92 174.99	50 Sn 118.70	51 Sb 121.76	52 Te 127.61	53 I 126.91	76 Os 190.2 77 Ir 192.2 78 Pt 195.09
7	86 Rn 222	87 Fr (223)	88 Ra 226.05	89 Ac 227	90 Th 232.05	91 Pa 231	92 U 238.07	93 Np (237)	94 Pu (242) 95 Am (243) 96 Cm (243)

Herein lay a weighty confirmation of Mendeléeff's principles of classification, and a method of assigning atomic number independent of chemical means. Moreover, gaps in the linear plot gave a welcome and infallible indication of elements still to be discovered. As we shall see in the next chapter, the atomic number, by prescribing the number of electrons contained in an atom, implies also its possible valency. The periodic system is thus seen to be based on the single property of atomic number, which through the implied electronic disposition decides the chemical character of an element.

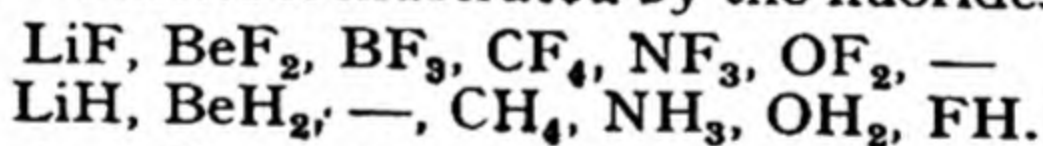
Long and Short Series. The periodic series, terminated by successive inert elements, comprise the following numbers of elements:

Series	Elements	Series	Elements
1 H, He	2	4 K—Kr	18
2 Li—Ne	8	5 Rb—Xe	18
3 Na—Ar	8	6 Cs—Rn	32
		7 Fr—	—

There is no general 'law of octaves' such as Newlands had sought to establish. The series are usually distinguished as 'short' (1, 2, and 3) and 'long.' The series lengths are represented by the quantity $2n^2$ where n has the successive values 1, 2 (twice), 3 (twice), and 4, a regularity that is a direct consequence of the electronic constitution of atoms (Chapter IX).

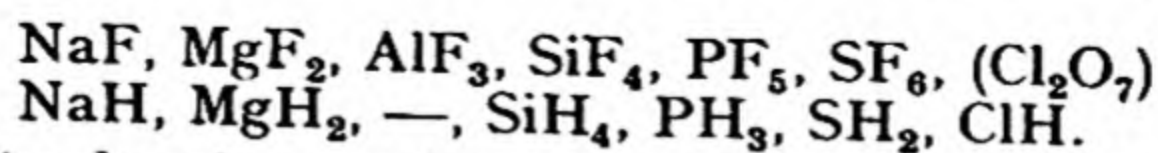
Survey of the Series.

1. The existence of this very short period is fully explained by the electronic constitution of its two members.
2. The order of valencies is illustrated by the fluorides and hydrides:



Each element of the series shows only a *single* valency, which rises to a maximum of IV with carbon, round which the lower valencies are symmetrically grouped. The elements display a steady change in type from the electropositive metals Li and Be to the highly electronegative O and F.

3. The succession of valencies in the fluorides and hydrides is as follows:



In the steady change from electropositive metal to electronegative halogen, and in the order of valencies towards *hydrogen*, Series 3 closely resembles the preceding series: to F (or O), however, valencies rise continuously to a maximum of VII.

4 and 5. The striking feature of these 'long' series is the preponderance of metallic elements, the change to non-metallic type being delayed until the concluding four elements—Ge—Kr; Sn—Xe—are reached.

Both Ge and 'grey' tin have the same (macromolecular) structure as diamond (p. 413). Other features common to these series will be exemplified from Series 4:

(i) Nearly all the compounds of the metals Ti—Cu^{II} are brightly coloured, whereas those of K—Sc, Cu^I—Br, and of the elements in Series 1–3 are nearly all colourless.

(ii) *Magnetic properties* of elements and compounds have the same selective distribution as colour in compounds.

(iii) Although the metals Ti—Mn inclusive each show an extensive series of lower valencies, a maximum is reached in the group values, i.e. Ti^{IV}, V^V, Cr^{VI}, Mn^{VII}. Mendeléeff therefore felt justified in placing them respectively in the regular succession of groups, but the succeeding metals, Fe, Co, and Ni, set by him in a Group VIII, posed a problem. He introduced the term 'transitional' for these members of Group VIII, conceiving that they formed a link between the regular Group VII(A) and the succeeding Group I(B). Modern knowledge of atomic constitution has clarified the situation, and the whole succession Ti—Cu^{II} (Zr—Ag in Series 5) inclusive is now termed 'transitional.'

If we exclude the 'transitional' metals and write

I	II	III	IV	V	VI	VII
K	Ca	Sc				
	Zn	Ga	Ge	As	Se	Br,

we see an arrangement not dissimilar to the 'short' Series 3.

6. This series repeats the characteristics of earlier Series 4 and 5, with the addition of the fourteen so-called 'rare earth' metals lying between ₅₇La and ₇₂Hf. All these metals show a well-developed tervalency, and an exceptionally close similarity in general chemical properties. They might be regarded as marking a sort of delay in leaving Group III for Group IV, ultimately reached at quadrivalent Hf.
7. This series is incomplete, although it has been notably extended in recent years by the addition of 'man-made' elements (p. 100).

Division of Groups into A and B Families. If we write out in order of atomic number the thirty-six elements between K and Xe, i.e. Series 4 and 5, we find the valency range I to VII repeated four times, viz. K—Mn, Cu—Br, Rb—Tc, Ag—I. There are two pairs of elements in each valency group, of which we may consider as examples:

K	Cu	Cr	Se	Mn	Br
Rb	Ag	Mo	Te	Tc	I
I(A)	I(B)	VI(A)	VI(B)	VII(A)	VII(B)

It is obvious that, while in each pair the elements are closely related, the pairs marked A diverge markedly in chemical properties from those marked B. The distinction so necessitated in the later groups is carried up into the earlier short series, so as to secure the most satisfactory gradation of properties in a group. Thus while Li and Na should obviously be placed above K and Rb, i.e. in the I(A) family, C and Si have far closer relationship to Ge and Sn in Group IV(B) than to the metals Ti and Zr in Group IV(A), and there can be no doubt that F and Cl should be in Group VII(B) above Br and I.

Atomic Size as a Periodic Property. The German chemist **LOTHAR MEYER** (1830-95), without knowledge of Mendeléeff's work, proposed in 1871 a very similar periodic classification, based upon *gram-atomic volume*, defined as

$$\frac{\text{Gram-atomic weight}}{\text{Density in gram per c.c.}}$$

At that time this was the only known general property related to atomic size, but the relation even for solid elements cannot be direct, since density depends on how closely the atoms are packed as well as upon their weight: as we now know, atoms of non-metals are much less densely packed than the atoms of most metals. However, atoms of similar elements tend to be similarly packed, and on this Lothar Meyer's success depended. In the plot of gram-atomic weight against gram-atomic volume (Fig. 24) the latter appears as a periodic property for which the alkali-metals define the successive 'waves,' corresponding with Mendeléeff's periods.

Below (in Å) are the atomic radii (p. 53) for Series 2-4:

Li	Be	B	C	N	O	F
1.52	1.12	0.87	0.77	0.74	0.73	0.72
Na	Mg	Al	Si	P	S	Cl
1.86	1.60	1.43	1.17	1.10	1.06	0.99
K	Ca	Sc	[Ti — Cu]			
2.31	1.96	1.60	[1.46 — 1.28]			
	Zn	Ga	Ge	As	Se	Br
	1.35	1.25	1.22	1.21	1.16	1.13

A plot of atomic radii against atomic number reveals a series of 'half waves,' with maxima at the alkali-metals (as in Meyer's curves) and minima at the halogens. The upward-turning portions in Fig. 24 are attributable to the less dense packing in solid non-metallic elements.

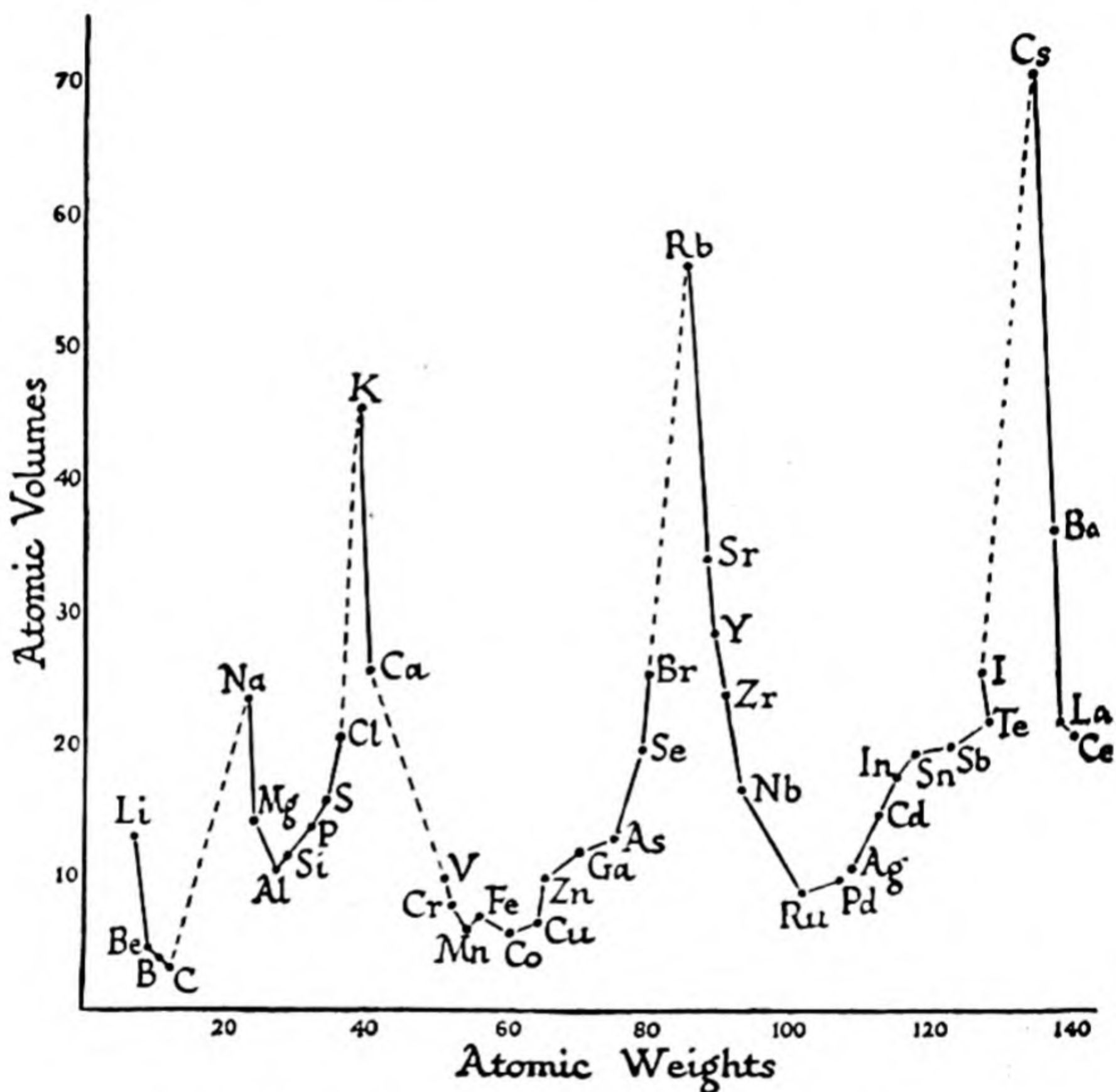


FIG. 24. ATOMIC VOLUME CURVE (after Lothar Meyer)

The Terrestrial Distribution of the Elements. The secular processes which have led to the present distribution and abundances of the elements in the earth's solid crust (or *lithosphere*) and in its gaseous atmosphere are based on the likeness or contrast between the general chemical behaviour of elements reflected and codified in their classification. The progress of geochemistry during the past half-century has enabled us to place some confidence in the table of

abundances given below in terms of *atomic percentages*. Let us suppose, to illustrate the calculation of atomic percentage, that the earth's crust consisted of only the four most abundant elements—oxygen, hydrogen, silicon, and aluminium—present respectively in the percentages by *weight* w_1 , w_2 , w_3 , and w_4 . Then the total number of gram-atoms per 100 gm. is

$$\frac{w_1}{16} + \frac{w_2}{1.0} + \frac{w_3}{28.1} + \frac{w_4}{27} = n,$$

and atomic percentages are found by multiplying the number of gram-atoms, e.g. $\frac{w_1}{16}$, etc., by $\frac{100}{n}$.

	Atomic Percentage	Atomic No.		Atomic Percentage	Atomic No.
Oxygen	54	8	Calcium	1.5	20
Silicon	16	14	Magnesium	1.4	12
Hydrogen	16	1	Potassium	1.1	19
Aluminium	4.8	13			
Sodium	2.0	11	Titanium	0.17	22
Iron	1.5	26	Chlorine	0.10	17

Each of the following elements is not more abundant than the stated *weight* percentage:

Carbon, phosphorus, sulphur, zinc, nickel	1×10^{-1}
Copper, lead, boron	1×10^{-2}
Tin, bromine	1×10^{-3}
Silver, gold, platinum, mercury, iodine	1×10^{-7}

Attention may be called to the following points:

- (1) Only four light elements—*hydrogen, oxygen, silicon, and aluminium*—form 91 per cent of the earth's periphery. By assuming that hydrogen, silicon, and aluminium are present as their oxides, water, silica, and alumina, 87 per cent of the oxygen is accounted for.
- (2) There is a marked fall in abundance after potassium; the preceding elements have atomic numbers not greater than 26.
- (3) Many elements regarded as common, e.g. copper, lead, tin, mercury, boron, and phosphorus, are in fact very scarce. They are economically accessible only because in geological time they have become segregated in highly localized deposits, or *ores*.

'Artificial' Elements. Four of the gaps left in the original periodic system have remained empty until the recent discovery of nuclear reactions and the building of machines, such as the cyclotron,

to induce them. These places have now been filled by the following elements:

Technetium, Tc, No. 43, between manganese and rhenium in Group VIIA;

Promethium, Pm, No. 61, one of the rare-earth metals;

Astatine, At, No. 85, the heaviest halogen;

Francium, Fr, No. 87, the heaviest alkali-metal.

The cost of production of even minute amounts of these elements is high, and in addition all but technetium are highly radio-active in the forms at present known: francium has a half-life of only 20 minutes. In spite of such heavy handicaps much of the chemistry of technetium and astatine is now explored and shown to accord with their positions in the periodic system.

The production of metallic elements heavier than uranium—the *transuranic elements*—by nuclear reactions is discussed in Chapter IX.

CHAPTER IX

ATOMIC CONSTITUTION

(I) ELECTRONIC STRUCTURE

Though rear'd upon the base of outward things,
These, chiefly, are such structures as the mind
Builds for itself. WORDSWORTH.

Atomic Spectra. No one who has practised the flame tests of qualitative analysis can fail to know that when given energy by sufficient rise of temperature the atoms of many metals emit coloured light (e.g. sodium, potassium, barium, copper, etc.). Similar knowledge is even more readily gained by walking after dark in the streets of our towns when coloured light radiated (here by electrical excitation in gas discharge tubes) from gases such as neon and argon, and by sodium and mercury, is all too evident. On analysis by passing it through the slit and prism of a spectrograph the coloured light appears as a *spectrum* of lines extending through the region of colour visibility and, as fuller investigation shows, into the invisible ultra-violet. The pattern of these lines is so characteristic of an element that spectrographic analysis is by far the most sensitive and certain means of its recognition, and many new elements were so discovered. The strong blue line in the spectrum of *indium* suggested its name, and of *thallium* its discoverer, Crookes, wrote '... from the Greek *thallos*, a budding twig, which I have chosen because the green line in its spectrum recalls the colour of spring vegetation': all the inert gases were recognized by their distinct spectra (p. 271).

Wave-length and Frequency. The position (or colour, when the visible spectrum is concerned) of each spectral line is fixed by the *wave-length* of the light waves producing it. For example, from a discharge tube containing hydrogen the spectrum of atomic hydrogen appears as sketched in Fig. 25.

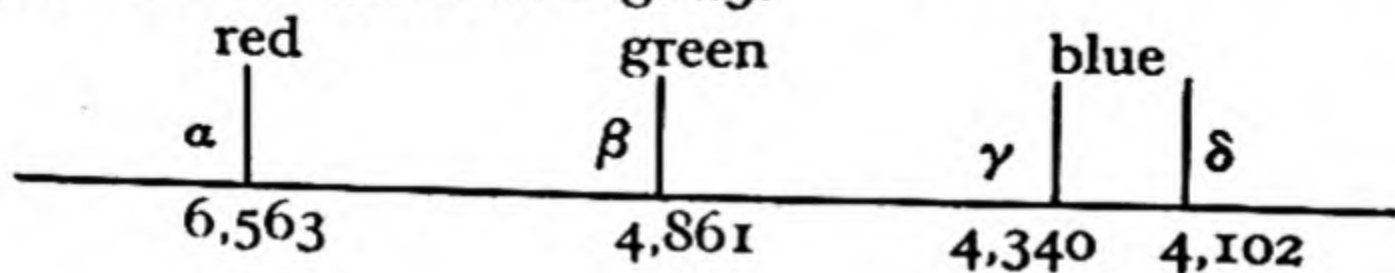


FIG. 25

The red line is the most intense, so that the light from the tube has a brilliant red colour not unlike that of the too familiar advertising device, the neon discharge tube. Wave-lengths are expressed, as in the above figure, in Ångstrom units (10^{-8} cm., p. 52). Light waves of all wave-lengths travel at the same fixed speed, very close to 3×10^{10} cm. per sec. Hence the distance travelled in one second contains

$$\frac{3 \times 10^{10}}{6,563 \times 10^{-8}} = 4.6 \times 10^{14}$$

wave-lengths of the red hydrogen light, and this number of wave-lengths passes a fixed point in the track of the light during every second. It is termed the *frequency* of the light. Wave length (symbol λ) and frequency (symbol ν) are interconvertible by the relation:

$$\begin{aligned} \text{Wave-length} \times \text{frequency} &= \text{Velocity of light} \\ &= 3 \times 10^{10} \text{ cm. per sec.} \end{aligned}$$

The position of a spectral line can thus be fixed not only by a wave-length but also by the corresponding frequency.

Bohr's Theory. From the vast labours of spectroscopists over half a century it emerged that the spectral frequencies for a given element could be arranged in several numerical series, expressible by simple formulae. Such series were named *sharp* (*s*), *principal* (*p*), *diffuse* (*d*), and *fundamental* (*f*), the descriptions being purely empirical and derived partly from the appearance of the lines (sharp, diffuse) and partly from the ease of excitation: only the principal series of an element is usually seen in flame tests. The devotion of spectroscopists is commemorated by the survival of the symbols *s*, *p*, *d*, and *f* in the modern nomenclature of atomic structure (p. 92).

At the end of the first decade of this century, in one decisive advance, these discoveries were brought to final fruition. Resting his ideas on the threefold basis of the proof given by Thomson in 1897 that the atoms of all elements contained the small negatively charged *electrons*; the later discovery (p. 97) by LORD RUTHERFORD (1871–1937) that the positive charge balancing these negative charges is concentrated in an extremely minute *nucleus* (radius 10^{-12} cm.); and lastly the *quantum hypothesis* announced (1900) by MAX PLANCK (1858–1947), the Danish physicist NIELS BOHR (1885–1962) arrived at a theory of the origin of line spectra, and thence a conception of atomic constitution that has since been amplified but has undergone no essential change.

The Hydrogen Atom. It was reasonable to suppose that the lightest atom contained the smallest possible number of fundamental particles, that is one electron and a balancing nucleus with equal but

positive charge, which came to be called the *proton*. The energy of the two particles is just $-\frac{e^2}{r_0}$, the potential energy of electron and proton separated by a distance r_0 . The negative sign arises because to separate the particles, i.e. *ionize* the atom, and bring the potential energy to zero requires an input of energy $\frac{e^2}{r_0}$. Now the emission of spectra occurs in circumstances favouring uptake of energy, and the only apparent way in which the atom can absorb energy is by the electron receding to a greater distance r_1 from the nucleus, when the potential energy increases to $-\frac{e^2}{r_1}$. The now 'excited' atom may regain its original energy and stability by radiating the excess energy as light. This very simple picture explains the radiation of light energy but gives no hint of why the light should be confined to definite and characteristic frequencies: nor does it explain the fundamental difficulty that the radius of the nucleus being only 10^{-12} cm. while the atomic radius is some 10,000 times greater (10^{-8} cm.) the electron can remain at such a distance from the attracting nucleus. This problem is only partly solved by the assumption that the electron rotates in an orbit round the nucleus, so that the outward drive of centrifugal force balances the inward pull of electric force.

If we looked edgewise at the plane of its orbit we should see the electron apparently travelling to and fro with a definite frequency along a diameter of the orbit. Such a regular oscillation of an electrical particle relative to another of opposite charge must, according to classical physics, originate electromagnetic radiation: the atom would continually lose (radiant) energy and the electron ultimately fall into the nucleus. Bohr therefore took the bold step of breaking away from classical physics by assuming that the electron in its orbit could not radiate. Whence then came the spectral frequencies? Fortunately Planck's hypothesis lay ready to hand.

The Quantum Hypothesis. Planck's original postulates took the following form:

(1) Emission and absorption of radiant energy by matter does not take place continuously but in finite *quanta* of energy.

(2) The quantum of energy is proportional to the frequency of the radiation

$$E_q = h\nu.$$

The constant of proportionality h is now appropriately known as *Planck's constant*. As a numerical example of the application of the hypothesis we calculate the energy absorbed by a mole of

substance of which each atom or molecule has absorbed one quantum of (blue) light of wave-length 4,000 Å.

$$N E_q = N h \nu \quad (N = \text{the Avogadro number})$$

$$N = 6.0 \times 10^{23} \quad (\text{p. 54})$$

$$\nu = 7.7 \times 10^{14} \quad (\text{sec.}^{-1})$$

$$h = 6.6 \times 10^{-27} \quad (\text{erg. sec.})$$

The energy absorbed per mole is therefore 30×10^4 joules, or 70 kcal. (p. 68). Such calculations necessarily play a very important part in the study of *photochemistry*.

Application of the Quantum Hypothesis. Bohr conceived that in a hydrogen atom the electron can adopt only certain (non-radiating) orbits of fixed, predetermined dimensions, in each of which the electron-proton system is in a 'stationary state' with a definite and specific energy, being the sum of the potential energy $-\frac{e^2}{r_n}$ and the kinetic energy of the electronic rotation. When the electron passes from an orbit of energy E_1 to another of energy E_2 it radiates a quantum of value $(E_1 - E_2) = h\nu$, if E_1 is greater than E_2 , or absorbs the same quantum if E_2 is greater than E_1 : the frequencies ν so defined are the observed spectral frequencies. The principle is that '*an atom can only release or absorb energy by transitions between stationary states*' (Fig. 26).

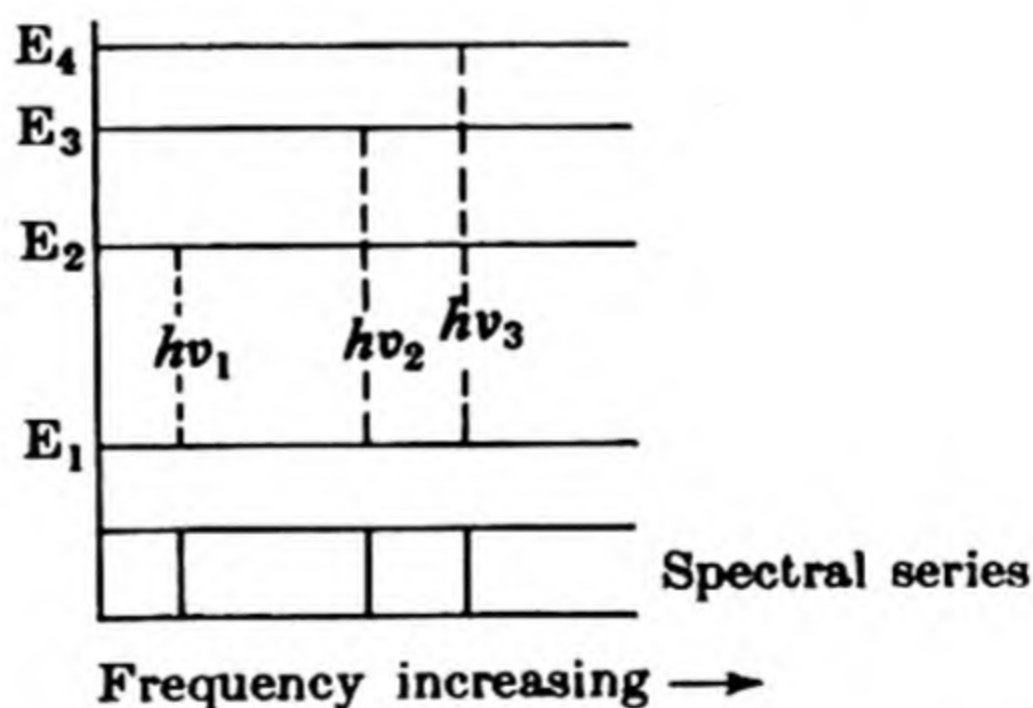


FIG. 26

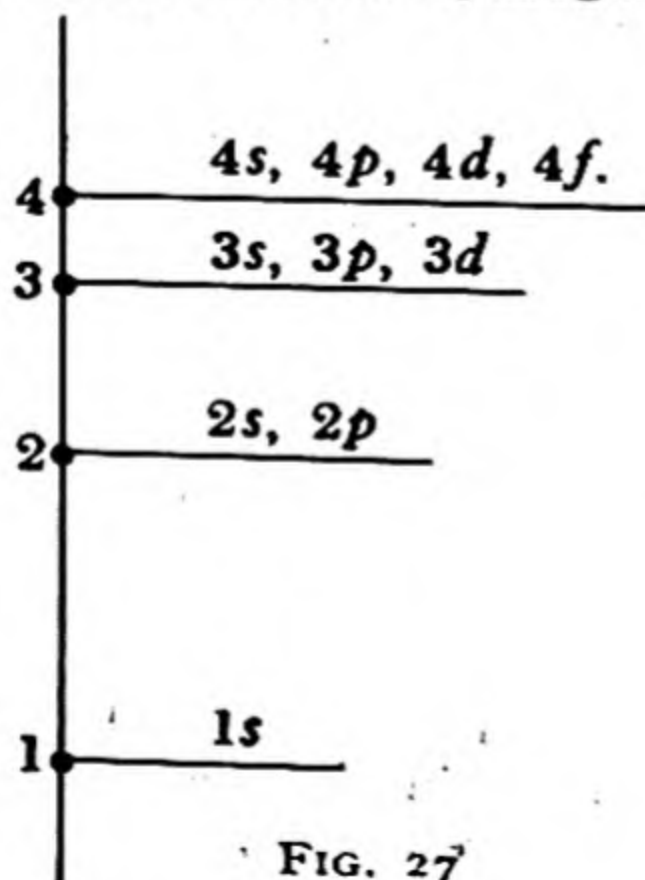
In a normal hydrogen atom the electron occupies the orbit of minimal energy and is then in its most stable or *ground* state. The less stable orbits of higher energy correspond to '*excited*' states: the successive discrete atomic energies are termed the *energy-levels* of the atom. The spectral frequencies for hydrogen (and for all other atoms) are fixed and immutable: on this depends the certainty of spectroscopic recognition of an element, previously mentioned. It

must follow that the discrete electronic orbits postulated by Bohr are equally immutable atomic characteristics.

It was difficult for contemporary physicists to accept the view that the spectral frequencies appeared to have no vibrational counterparts within the radiating atom, but the fertility of Bohr's conception (amplified but not radically altered in later years) when applied to atoms in general has long since dispelled doubts of its truth. The influence of the train of ideas originated by Bohr on the progress of chemistry in this century has at least equalled that of the final acceptance of Avogadro's principle at the middle of the last century.

Wave (or Quantum) Mechanics. From its inception about 1900 the quantum theory has steadily developed into a whole new physical science of 'wave mechanics,' which embraces and makes intelligible such phenomena as the diffraction of particles (p. 51). Bohr could deduce the energy levels in hydrogen from its spectrum, but only as empirical facts, without a rational explanation of their existence to the exclusion of all other states of energy. The new science provided a general mathematical theory from which the levels can be successfully predicted and so made intelligible, at least from a mathematical standpoint. The new theory goes further, and yields algebraic expressions in terms of rectangular co-ordinates, x , y , and z passing through the centre of the atom, for the possible types of orbit associated with each energy level. These *orbital functions* (usually abbreviated to 'orbitals') are not simple to interpret, but for our purpose we shall need to know only the number of such orbitals at each level.

Energy Levels and Orbitals in the Hydrogen Atom.



In Fig. 27 four successive levels are distinguished by the numbers 1-4, the first corresponding to the ground state of the atom. The series of levels continues upwards until terminated by the *ionization level*, at which the atom has enough energy to separate the electron completely from the proton. It is characteristic of levels in all atoms that the energy difference between contiguous levels becomes less the higher the energy.

Distinct types of orbitals are distinguished by the literal symbols *s*, *p*, *d*, and *f* (cf. p. 88), and a new type appears at each successive level. These different types of orbitals are common to all other atoms, where, as we shall see in a later section, their distinction is of paramount importance. The constitution of the hydrogen atom is so simple that the new mechanics when applied to it can yield exact algebraic expressions for them, which can be carried over to atoms heavier than hydrogen. The simplicity of the lightest atom has, however, the further consequence that the electron may occupy any of the types of orbital prescribed for a given level without change in the atomic energy: in this sense all orbitals at a given level are *equivalent*, and for hydrogen the distinctions between types *s*, *p*, etc., lose practical importance.

Energy Levels and Orbitals in General.

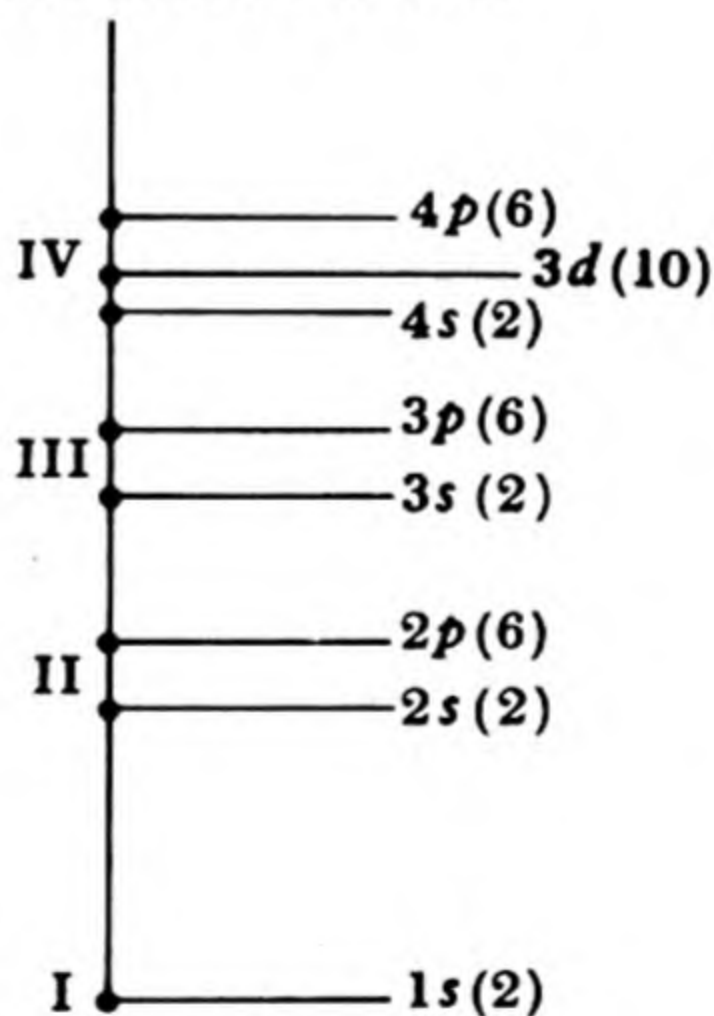


FIG. 28

In Fig. 28, which shows schematically the order of the energy states of atoms from helium to krypton inclusive (Series 1-4 of the Periodic System), we see a more complicated pattern of levels than

in hydrogen. The essential difference is that distinct types of orbital are associated with distinct energy levels: (*n*) *p* is always rather higher than (*n*) *s*, and 3*d* is so much above 3*s* or 3*p* that it lies between 4*s* and 4*p*. The numbers distinguishing levels in hydrogen lose some of their significance, but the levels in heavier atoms can still be grouped together as indicated by the Roman numerals in Fig. 28.

The Number of Equivalent Orbitals in a Type. At all levels in all atoms, including hydrogen, the symbol *s* implies only *one* orbital, but the other symbols, *p*, *d*, and *f*, comprise more than one:

Type	<i>s</i>	<i>p</i>	<i>d</i>	<i>f</i>
Equivalent orbitals	1	3	5	7

All orbitals under one symbol are *equivalent*, that is an electron may occupy any one of them without alteration in the atomic energy. In hydrogen alone orbits of *all* types under the same numerical symbol 1, 2, etc., specifying the energy level are equivalent.

Atomic Number. Moseley's researches on X-ray spectra (p. 78) were contemporary with Bohr's first expositions of his ideas on atomic constitution, and he was among the first to stress the significance of the number as giving the *number of electrons* and necessarily also the *nuclear positive charge* in an atom, an interpretation soon universally recognized.

The Exclusion Principle. In spite of all the knowledge of levels and orbitals recounted in previous sections, an attempt to formulate electronic configurations for atoms in general would be frustrated unless an answer were forthcoming to the question 'May more than one electron occupy the same orbital?' The *exclusion principle*, announced by the Swiss physicist PAULI (1900-58) in 1925, provides the answer.

If all atomic electrons were exactly alike and hence indistinguishable from one another there could be no more than one to each orbital. However, many atoms and ions possess magnetic properties which can only originate from the rotatory motions of atomic electrons. It has long been well known that an electric current (i.e. a stream of electrons) in a coiled conductor creates a magnetic field in the direction of the axis of the coil: an electron travelling in an orbit is no less an electric current, creating an atomic magnetic field. It is found that the purely orbital motions only very partially account for atomic magnetic properties, and some other type of rotatory motion is essential. This can only be a *spinning of the electron on its own axis*. Such spin can be clockwise or the opposite. The distinction conferred in this way is like that between left-hand and right-hand screws, from a mixture of which

the two sorts can always be picked out by inspection. Pauli's principle can be thus stated: one orbital can contain only as many electrons as are all distinguishable from each other, and this number is *two*, with opposed spins. The maximum number of electrons that can be allocated to a given orbital type under this rule is entered in parentheses on Fig. 28.

Electronic configurations.

Series 1 and 2 (H to Ne):

Atom	Atomic Number	Occupation of Orbitals				
		1s	2s	2p _x	2p _y	2p _z
Hydrogen	1	1				
Helium	2	2				
Lithium	3	2	1			
Beryllium	4	2	2			
Boron	5	2	2	1		
Carbon	6	2	2	1	1	
Nitrogen	7	2	2	1	1	1
Oxygen	8	2	2	2	1	1
Fluorine	9	2	2	2	2	1
Neon	10	2	2	2	2	2

The number of electrons, given by the atomic number, is allocated, under the operation of the exclusion principle, to the energy levels in Fig. 28 starting from the lowest, 1s, and working upwards. When two electrons are placed in one orbital they must have opposed spins, and when 2, 3, or 4 electrons are to be placed in 2p orbits the most stable condition (ground state) is attained when they are spread as widely as possible over the three orbits. The distinguishing suffixes *x*, *y*, and *z* for the three equivalent *p* orbitals are suggested by the mathematical expressions for them.

Series 3 (Na to Ar):

In the atoms of all members of this series the levels 1s, 2s, and 2p remain filled to the maximum reached in Ne, and the configurations in 3s and 3p follow exactly those in the 2s and 2p in the preceding Series 2.

Series 4 ('long series,' K to Kr):

In accordance with the diagram of Fig. 28, the orbital 4s fills first with K (4s) and Ca (4s²), which are then followed by ten 'transitional' elements (p. 82) resulting from the progressive filling of the next equivalent set of orbitals, 3d: scandium has the configuration

$4s^2 3d^1$ and zinc $4s^2 3d^{10}$. Finally the set $4p$ is completed with six more electrons, giving the configuration of Kr in which all orbitals in Fig. 28 are filled to capacity.

It will be seen that the Series 1-4 correspond exactly to the progressive filling of the grouped energy levels given Roman numerals in Fig. 28.

Ionization Potentials. When a beam of electrons formed in a discharge tube (Fig. 20, p. 49) passes from the cathode source through a grid at potential V volts, each electron is accelerated and finally acquires kinetic energy $e \times V$, expressed as V *electron-volts*. An electronic projectile so produced, encountering an atom, may transfer sufficient energy to an atomic electron to expel it from the atom, which thereby becomes a positive ion. The accelerating potential V_1 at the point where such ionization first begins to be detectable is termed the (first) *ionization potential* of the atom. To expel a second electron a higher grid potential V_2 is needed, and this is the *second* ionization potential, and so on. The series of potentials I, II, III gives the energy of formation (in electron-volts) of the positive ions A^+ , A^{2+} , and A^{3+} from an atom A , but only the potential I measures the energy of electron binding in the uncharged atom; to expel a second or third electron the energy to separate it from positive ions A^+ , or A^{2+} has also to be supplied. The sodium ion Na^+ must have the same electron arrangement as an atom of its neighbour neon (p. 94), but their potentials are very different— Na^+ , 47.0 eV; Ne, 21.5 eV. In what follows, ionization potential means the first potential, corresponding to the change $A = A^+ + e$.

In passing down any group of the Periodic System ionization potentials steadily and markedly decrease, while atomic size increases (p. 53).

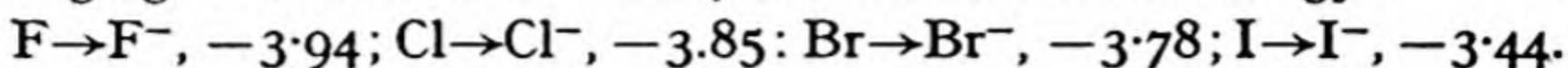
Li, 5.4	C, 11.2	F, 18.6	He, 24.5
Cs, 3.9	Sn, 7.3	I, 10.4	Xe, 12.1 (electron-volts).

We deduce an expected inverse relation between atomic size and potential, for the distance of the outermost electrons from the nucleus determines the size of an atom. Across a series of the Periodic System atomic size steadily *decreases* (p. 83), but the general increase of potential is modified in the progressive filling of the two types of orbital concerned:

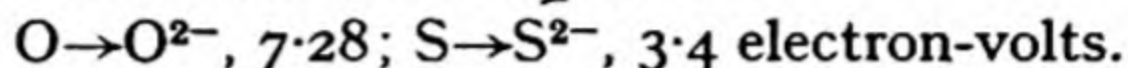
Na	Mg	Al	Si	P	S	Cl	Ar
5.1	7.6	6.0	8.1	11.1	10.3	13.0	15.7
s orbitals		p orbitals					

Electron Affinity. While for each of the halogens the input of energy to effect ionization such as $Cl = Cl^+ + e$ is little short of the maxima reached in the neighbouring inert elements, in the *addition*

of an electron to give an *anion*, e.g. $\text{Cl} + e = \text{Cl}^-$, energy is *released*. Using again the electron-volt as an atomic unit of energy:



These energies are termed the *electron affinities* of the halogens. To form doubly charged anions (for example O^{2-}) the second electron must be forced into an already negatively charged atom, and the total energy of their formation is positive:



We reach the conclusion that with the sole exception of the halogen anions the change (*in vacuo*) of all atoms into their ordinary ionized states is achieved only by the input of the large energies required to overcome the binding energies of their electrons.

The Electron-volt as a Unit of Energy. The (kinetic) energy acquired by an electron in passing through a potential difference of one volt is a very convenient and practical physical unit of atomic energy, but for comparative purposes in chemistry it is necessary to know how to convert electron-volts per atom (or molecule) into kcal. per gram-atom (or gram-molecule).

We have:

$$\text{Electrical energy (joules)} = \text{Quantity of electricity (coulombs)} \times \text{Potential difference (volts).}$$

Since a mole of electrons = 1 faraday = 96,500 coulombs

$$1 \text{ electron-volt per atom} \equiv \frac{96,500 \times 1}{4.18 \times 1,000} = \underline{23.0 \text{ kcal. per gram-atom.}}$$

Hence when an atom (or molecule) acquires one electron-volt a gram-atom (or gram-molecule) acquires 23.0 kcal.

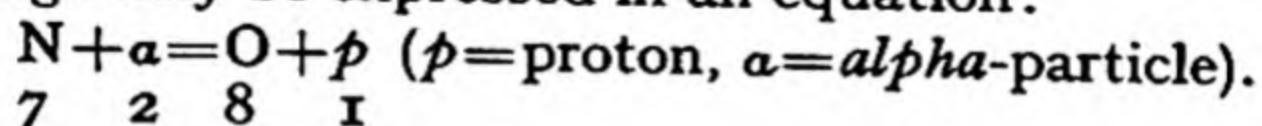
(2) NUCLEAR CONSTITUTION

Radioactivity. The atomic nucleus, although exceedingly minute compared with the atom which contains it, bears not only the total positive charge required to balance that of the atomic electrons but almost all the mass of the atom. The discovery of radioactivity by BECQUEREL (1852–1908) in 1896, and the subsequent isolation of salts of the radioactive metal radium by MME CURIE (1867–1934) and her husband PIERRE CURIE (1859–1906), enabled a detailed study of the phenomena of radioactivity to be undertaken (mainly under the aegis of Rutherford between 1900 and 1910). That a radioactive change differed from any known chemical reaction was dramatically proved by the observation that it proceeded with unchanged rate at the highest and lowest attainable temperatures, and independently of the chemical or physical state of the radium source. It soon became clear that the unstable atom

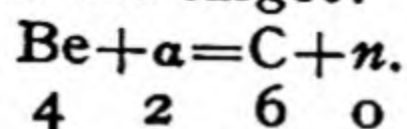
of radium spontaneously breaks down into atoms of lesser atomic weight, ejecting in that process two kinds of particles—*beta*-particles, identified as electrons, and *alpha*-particles, recognized as helium ions, He^{2+} . Although atoms chemically different from the parent are produced in both *alpha* and *beta* changes, only in the former is there a sensible change of mass, by 4 units. Radium (atomic weight 226) in a series of spontaneous changes involving among the intermediate steps the loss of 5 *alpha*-particles, generates finally (inactive) lead (atomic weight $206 = 226 - 5 \times 4$).

Nuclear Size. The two particles characteristic of the stages in this natural radioactivity are ejected from the active atoms with exceedingly high kinetic energies, and it was realized that the heavy *alpha*-particles provide a very powerful means for investigating the constitution of non-radioactive atoms. In 1911 Rutherford demonstrated that *alpha*-particles from radium pass through thin gold foil without change of velocity or direction, with the most significant qualification that 1 particle in about 100,000 is widely deflected and may even be reversed in direction. In such an experiment the electrons in the gold atoms would be unable to affect the tracks of the far more massive *alpha*-particles. It followed that the gold foil contained, in extremely sparse distribution, particles massive enough to reverse the direction of *alpha*-particles travelling with a kinetic energy of about 5 million electron-volts. Such particles could only be what were soon to be termed the *nuclei* of the atoms, with mass about 200 atomic weight units. The data gained from the experiments enabled the 'target area' of the nuclei to be estimated, and the diameter thence deduced was of the order 10^{-12} cm. (cf. atomic radius 10^{-8} cm).

Transmutation: Neutrons. Up to the year 1919 only *alpha*- and *beta*-particles had been recognized as the result of radioactive change. In that year Rutherford reported the first example of a genuine artificial 'transmutation'; when the nuclei of nitrogen atoms were assailed by fast-moving *alpha*-particles *protons* were ejected. The nuclear change may be expressed in an equation:

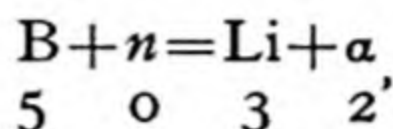


The atomic numbers beneath the symbols are seen to balance. Later, in 1932, Chadwick and Goldhaber carried out similar experiments with beryllium as the target:



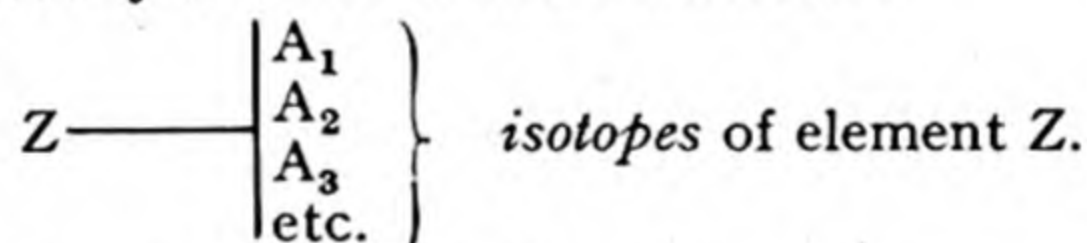
In this nuclear reaction, when beryllium was transmuted to carbon, a new particle, almost equal in mass to the proton but *with no net charge*, soon to be named a *neutron*, was proved to be produced.

Developments subsequent to these discoveries have been very rapid. The positive charge on the *alpha*-particle effectively prevents its close contact and interaction with any but the nuclei of atoms of low atomic number. On the contrary, a neutron penetrates any atom and interacts with its nucleus, by which it is commonly absorbed, to produce a heavier nucleus that may or may not be stable. The nuclear reaction of a neutron with a boron atom:



which yields the easily recognized *alpha*-particle, has been used to identify neutrons, which easily escape notice through their lack of charge.

Nuclear Constitution: Isotopes. All nuclei are now considered to be compounded of protons and neutrons. The number of protons, or the *atomic number* Z , decides the number of electrons and implicitly their particular distribution in orbitals (Table, p. 94); the atomic number therefore characterizes a particular chemical element, and conversely. The *mass number* A , given by $A = Z + N$ (neutrons), decides the weight of a nucleus. Since there need be no unique ratio between Z and N , to a given atomic number there corresponds usually a series of mass numbers:



The *isotopes* corresponding to the series of mass numbers have distinct atomic weights but identical electronic arrangement, and are therefore chemically indistinguishable. The following are some examples of the naturally occurring isotopic mixtures of common elements:

Chlorine: $Z = 17$

Mass numbers	35	37
Neutrons	18	20
Atomic weight	34.970	36.967
Percentage abundance	75.4	24.6
Chemical atomic weight	35.457	

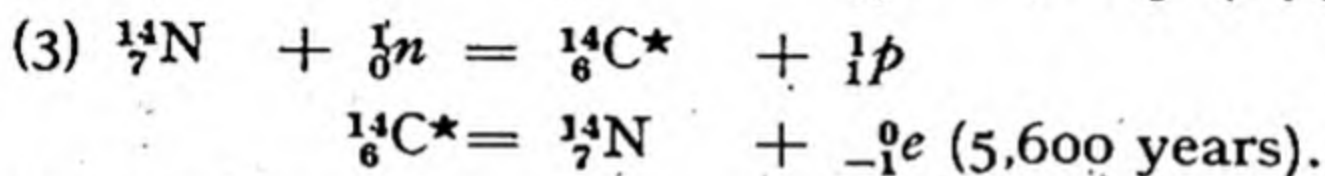
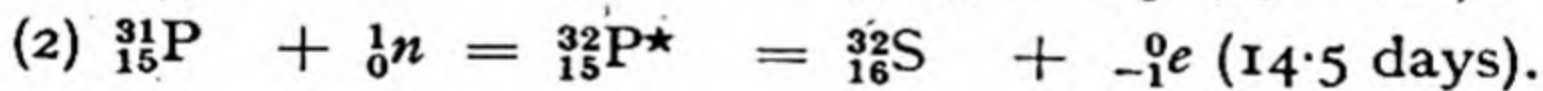
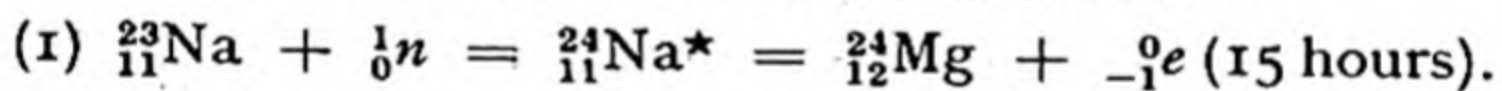
Magnesium: $Z = 12$

Mass numbers	24	25	26
Neutrons	12	13	14
Atomic weight	23.986	24.986	25.983
Percentage abundance	79.0	10.0	11.0
Chemical atomic weight	24.32		

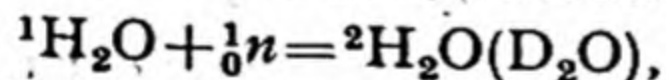
		Percentage abundance	
Hydrogen, ^2H (deuterium)		0.016	
Nitrogen, ^{15}N		0.36	
Oxygen, ^{18}O		0.20	
<i>Argon and potassium:</i>			
Z	^{18}Ar	^{19}K	
A	36	40	39
Percentage abundance	0.4	99.6	93
Chemical atomic weight	39.94		39.10

The widespread occurrence of isotopy was first revealed by the work of ASTON (1877-1945), using the earliest mass spectrograph, of his own design.

'Artificial' Radioactivity. By irradiating them with neutrons from that prolific source the atomic 'pile' (p. 100) many elements can be rendered unstable and therefore radioactive:



In these equations the mass numbers at the top left of the symbols and the atomic numbers below must separately balance. The sign * designates a radioactive form, and the period given after the equation is the 'half life' of the active decay, i.e. the time elapsed when half the active form has disappeared. In reactions of the simplest type (1) and (2) only radioactive enrichment can usually be achieved, but in the type (3), where there is change of atomic number, complete separation of the radioactive product is possible. Thus the activity of ^{14}C in the carbonate $^{14}\text{CO}_3^{2-}$ produced from nitrate NO_3^- can be recovered as $^{14}\text{CO}_2$ by acidification. Radioactive light elements produced by the atomic pile have proved of great service in radio-therapy, and as 'tracer' elements in elucidating the finer details of chemical reactions. Water has advantages over graphite as a 'moderator' in a pile (p. 101), but owing to the vigorous absorption of neutrons in the reaction

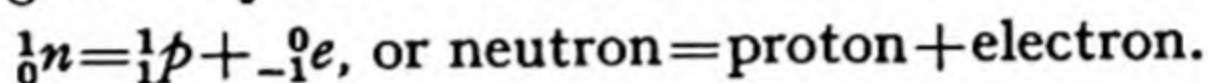


only deuterium oxide ('heavy water') can be applied to this purpose.

Stability of Nuclei. A review of the stable species, or *nuclides*, of the ninety-two elements between and including hydrogen and uranium discloses the following numerical relations between protons (Z) and neutrons (N) in their nuclei:

	$A = Z + N$			Nuclides	Percentage
(a)	even	even	even	164	59.0
(b)	odd	even	odd	56	20.1
(c)	odd	odd	even	52	18.7
(d)	even	odd	odd	6	2.2

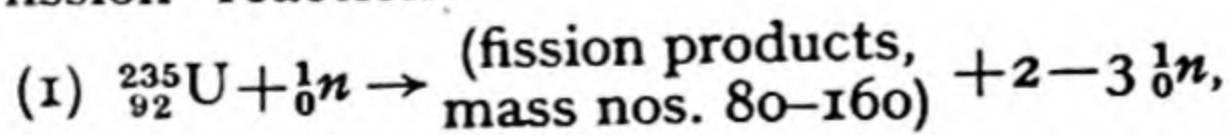
It may therefore be assumed that the relation (a), with Z and N both even, gives nuclides of the greatest stability, and that a relation (d) tends to instability, with consequent radioactivity, in which stability is gained by the nuclear reaction:



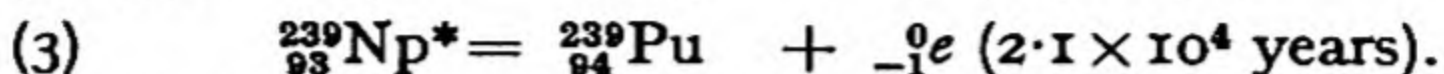
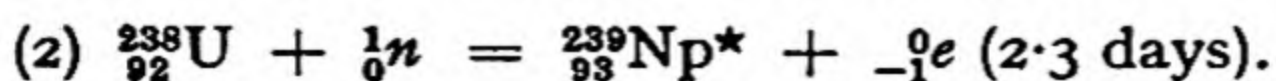
Exceptions to this rule are found only in the lightest elements, of which four contribute to the small class (d), viz. ${}_1^2\text{H}$, ${}_3^6\text{Li}$, ${}_5^{10}\text{B}$, and ${}_7^{14}\text{N}$; in all these nuclides $Z=N$.

In the Periodic System, elements in even-numbered Groups O, II, IV, VI, and VIII must have even atomic numbers Z , and since the table shows that these elements provide 79.1 per cent of all naturally occurring nuclides it follows that they must each have numerous isotopic forms (e.g. Ca has six and Sn ten isotopes). Elements of odd atomic number lie in the odd-numbered groups, and yield only 20.9 per cent of all nuclides: hence in these groups few isotopic species are found, and indeed a number of these elements have only a single (naturally occurring) atomic species (e.g. ${}^{19}\text{F}$, ${}^{23}\text{Na}$, ${}^{27}\text{Al}$, ${}^{31}\text{P}$).

The Atomic Reactor: Transuranic Elements. A typical form of reactor consists essentially of a large number of aluminium canisters each containing a cylindrical uranium 'slug,' and embedded at regular intervals in a stack of blocks of very pure graphite. The whole assembly is contained in stout concrete walls, and cooled by air blown through channels in the 'pile.' The operation of such a reactor depends on the presence in natural uranium (consisting mainly of the very feebly radioactive nuclide ${}^{238}\text{U}$) of about 0.7 per cent of the isotope ${}^{235}\text{U}$. Unlike ${}^{238}\text{U}$ the latter undergoes a spontaneous 'fission' reaction:



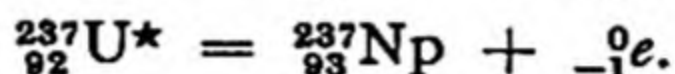
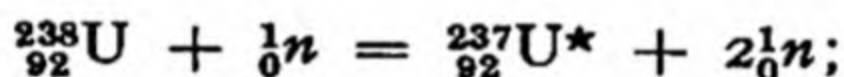
with a gain of 1-2 neutrons. Further nuclear reactions consequent upon this release of neutrons lead to the production in nearly stable form of the transuranic element *plutonium*, ${}_{94}\text{Pu}$:



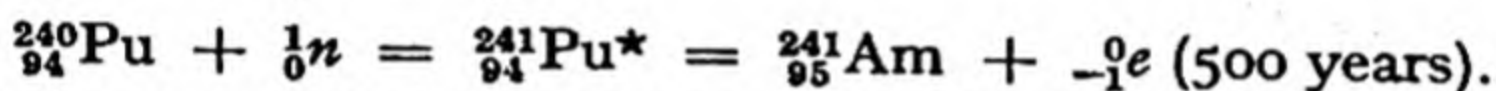
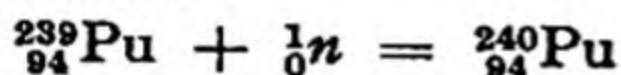
These reactions would not occur unless the high velocities of the neutrons when ejected from the reaction (1) were reduced by elastic collisions with carbon atoms in the graphite 'moderator' (see also p. 99).

When the fission products of (1) and the metal plutonium from (2) and (3) have sufficiently accumulated in the uranium 'slugs', these are withdrawn and processed by chemical means for the recovery of uranium and its products. From the fission of ${}^{235}\text{U}$ the most important elements recovered are ${}^{137}\text{Cs}$ and ${}^{90}\text{Sr}$, both of which are radioactive and now much employed in radio-therapy.

Another, secondary, reactor process, leading also to regeneration of neutrons, is:



The first transuranic element, *neptunium*, Np, is thus obtained in a nearly stable form (half-life 2.2×10^6 years), in contrast with the short-lived nuclide ${}^{239}\text{Np}$ of reactions (1) and (2). The third transuranic element *americium*, Am, is produced in limited amounts by the reactions:



All the elements listed in the equations above are radioactive, but the sign * has been reserved for those of short life. Small amounts of the fourth transuranic, *curium*, in the form ${}_{96}^{242}\text{Cm}$ (162 days) can also be isolated from pile products. The two further transuranic metals at present known, *berkelium*, ${}_{97}\text{Bk}$, and *californium*, ${}_{98}\text{Cf}$, both of which are strongly radioactive with short half-lives, are obtained in minute amounts from processes in the cyclotron.

Other 'Artificial' Elements. Of the elements between hydrogen and uranium four are known only as products of appropriate nuclear reactions. They are as follows:

Technetium, Tc, Group VII(A) (10^6 years):

Promethium, Pm, rare-earth metals (2.5 years).

Astatine, At, heaviest member of the halogen group, Group VII(B), (8.5 years).

Francium, Fr, the heaviest alkali-metal (20 minutes).

Much of the chemistry of the nearly stable metal Tc has been explored, and it is known that At resembles the halogens in forming the anion At^- .

CHAPTER X

CHEMICAL COMBINATION AND VALENCY

Historical. The publication in 1800 by VOLTA (1745–1827) of an account of what we now call a voltaic cell (Chap. XVIII) put for the first time into the hands of chemists an easily set-up source of steady electrical current, which they were not slow to exploit. One of the first and most brilliant achievements of the new method of *electrolysis* was the isolation (1808) by Davy of the alkali- and alkaline-earth metals (Na, K; Ca, Sr, Ba), which he accomplished by passing electric current through fused sodium or potassium hydroxides, and through the fused chlorides of the other metals. The generalization that the passage of electricity through an aqueous salt solution undoes the chemical action giving rise to the salt was probably first clearly expressed by Berzelius. In one of his own experiments (1803) he showed that when 'sulphate of soda,' obtained by treating 'soda' with sulphuric acid, is electrolysed in aqueous solution 'soda' accumulates around what was later to be called (by Faraday) the *cathode*, and sulphuric acid around the oppositely charge *anode*. It appeared to Berzelius that chemical action must therefore have an electrical basis, and he developed this conception in his *dualistic theory*, which required elements and compounds to be distinguished as either positively or negatively charged: chemical union was promoted and sustained by electrical attraction. On his death in 1848 he had not overcome the numerous difficulties and contradictions emerging from the application of his theory, nor been able to extend it acceptably into the then rapidly expanding field of organic chemistry. Nevertheless we must accord to Berzelius the first attempt to formulate a workable theory based on the principle that chemical combination is an electrical phenomenon.

The discovery of *valency* as an atomic property (1852 onwards), which we owe to Frankland, rested upon an empirical basis of chemical composition; and when Frankland showed by such means that chlorine could replace hydrogen atom for atom (since both were 'monads,' or univalent) he was dealing a shrewd blow at Berzelius's theory, which, however, had survived an earlier assault of the same kind by Dumas, who based his case on the facts of organic chemistry. In the dualistic theory hydrogen and chlorine belonged to the opposite categories of positive and negative elements, and it was inadmissible that they should play

a similar chemical role. Principally under the leadership of Kekulé, exercised from 1858 onwards, the conception that the combining powers of carbon, nitrogen, and oxygen were normally and constantly subdivided into 4, 3, and 2 parts respectively, and that the powers of hydrogen and chlorine were indivisible, brought into organic chemistry a novel and beautiful simplicity. In the words of SIR WILLIAM TILDEN (1912): 'We have a universally acknowledged system of formulae based on valency, which we define as *the habit in regard to combination exhibited by atoms, without forming any hypothesis of the nature of (chemical) affinity.*'

There is an element of irony in the modern developments, in which the preceding historical sequence has been almost reversed. To the many followers of Berzelius, whose theory purported to explain chemical union as that of *unlike* and oppositely charged atoms, the existence of such molecules as H_2 , O_2 , N_2 , etc., seemed impossible, and Avogadro's principle, which demanded them, was rejected for half a century, until Cannizzaro's vindication in 1860 (p. 27). To-day we find the most typical examples of (covalent) binding in these very molecules, and from a knowledge of its cause we project a consequential formulation of valency.

Ionic Compounds. It is easy to understand the nature of bonds which exist in a substance such as sodium chloride. In the reaction between elementary sodium and chlorine an electron is transferred from each metal atom to one of the halogen, and each atom becomes an ion, Na^+ and Cl^- . The product of the reaction is necessarily a *crystal*, composed of equal numbers of these ions, arranged in regular formation in the most stable possible way, i.e. unlike ions as close together as possible, and ions of like sign as far apart as possible. In the diagram (Fig. 29) of the structure of sodium

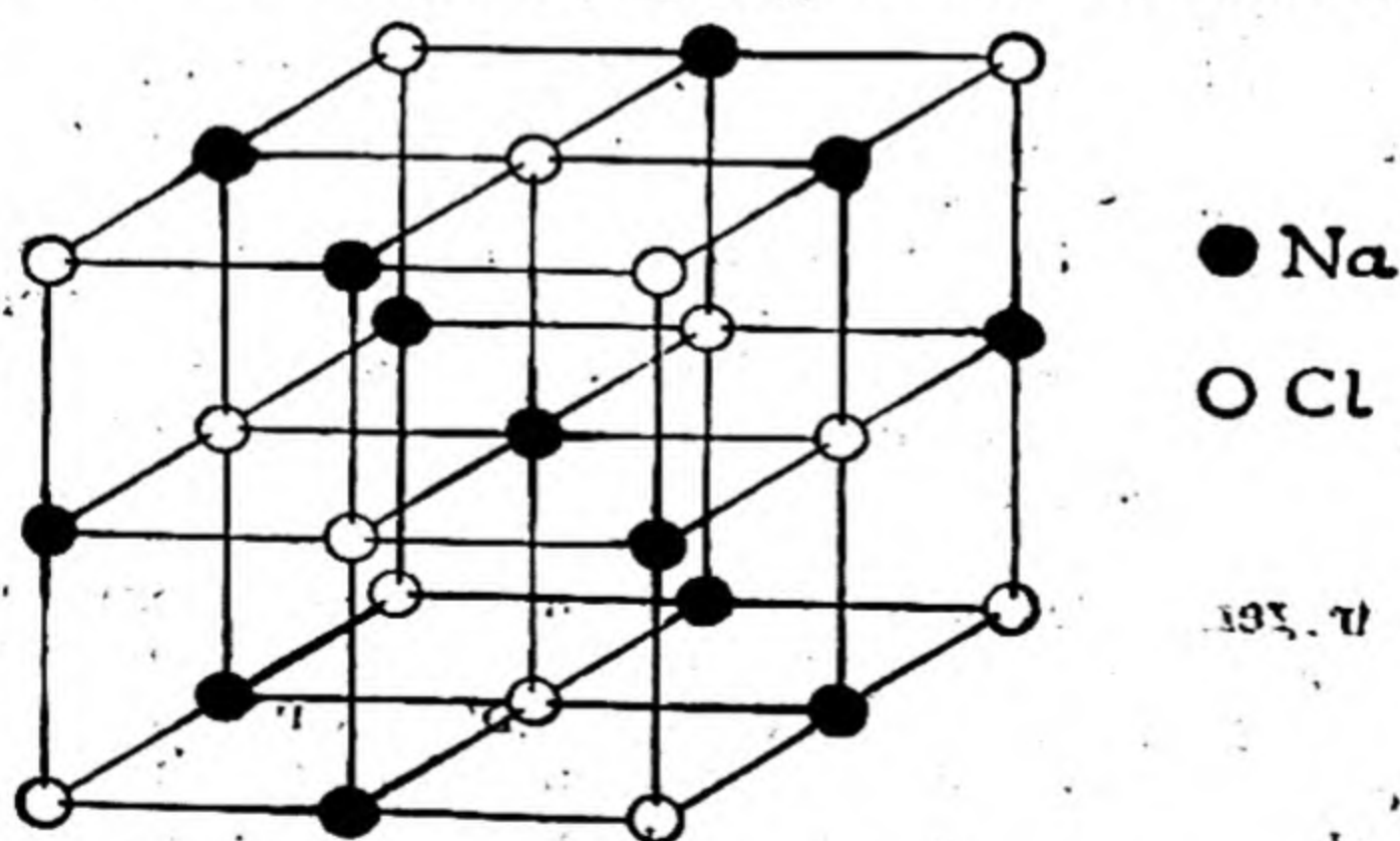


FIG. 29, SODIUM CHLORIDE CRYSTAL STRUCTURE

chloride the distance between centres of like ions is $\sqrt{2}$ times as large as that between unlike ions.

The formation of a crystal of an ionic compound may thus be regarded as consisting of two successive parts: (1) the formation of the separated, gaseous ions from the normal forms of the elements concerned; (2) the assembling of the ions in the crystal structure. An energy balance-sheet drawn up for the formation of sodium chloride is set out below:

	Heat change (ΔH , kcal.)	
(1) $\text{Na(s)} = \text{Na(g)}$ (sublimation of sodium)	+ 26	
(2) $\frac{1}{2}\text{Cl}_2 = \text{Cl(g)}$ (atomization of chlorine, p. 115)	+ 29	
(3) $\text{Na(g)} = \text{Na}^+(\text{g}) + e$ (ionization potential, p. 95)	+118 (5.11 eV.)	
(4) $\text{Cl(g)} + e = \text{Cl}^-(\text{g})$ (electron affinity, p. 95)		−88 (−3.85 eV.)
Totals	<u>+173</u>	<u>−88</u>
Net for production of gaseous ions	<u>+ 85.</u>	
(5) $\text{Na}^+(\text{g}) + \text{Cl}^-(\text{g}) = \text{Na}^+\text{Cl}^-(\text{s})$	<u>−183</u>	(lattice energy).
(6) $\text{Na(s)} + \frac{1}{2}\text{Cl}_2 = \text{NaCl(s)}$	<u>− 98</u>	(heat of formation).

As in the example given above, the process of ionization is highly *endothermic* for nearly all known ionic compounds, but is very greatly offset by the large release of energy on forming the crystal from the ions, termed the *lattice energy*, which measures the strength of bonding within the crystal. It will be clear that the units forming the crystal are never *molecules*. To produce a stable compound of this sort we need reactants of opposed nature: an *electropositive* element with low ionization potential, for example a metal (p. 95), and an *electronegative* element (or group of elements) tending to absorb electrons. We may expect this type of ionic binding, operating always in a solid crystal, to be typical of the large class of compounds called *salts*.

The Hydrogen Molecule. What we must seek to explain is how, when two atoms of hydrogen approach each other, energy is released and the atoms are thereby stabilized in that permanent state of contiguity we call the hydrogen molecule. In the reaction $2\text{H} = \text{H}_2$, $\Delta H = -104$ kcal. (see further p. 115), and the distance between atomic centres in the molecule is 0.74 Å.

In the diagram (Fig. 30) are seen, on the left, the ground energy level in the helium atom, occupied by two electrons in 1s orbitals: and on the right the coincident lowest levels of two hydrogen atoms, each occupied by one electron in a 1s orbital. The positions of these levels are accurately known from the atomic spectra of helium and hydrogen. The ground level of helium is necessarily deeper because the nuclear charge of helium is twice that of hydrogen. On the horizontal axis of the diagram the distance r between the hydrogen atoms is to be registered.

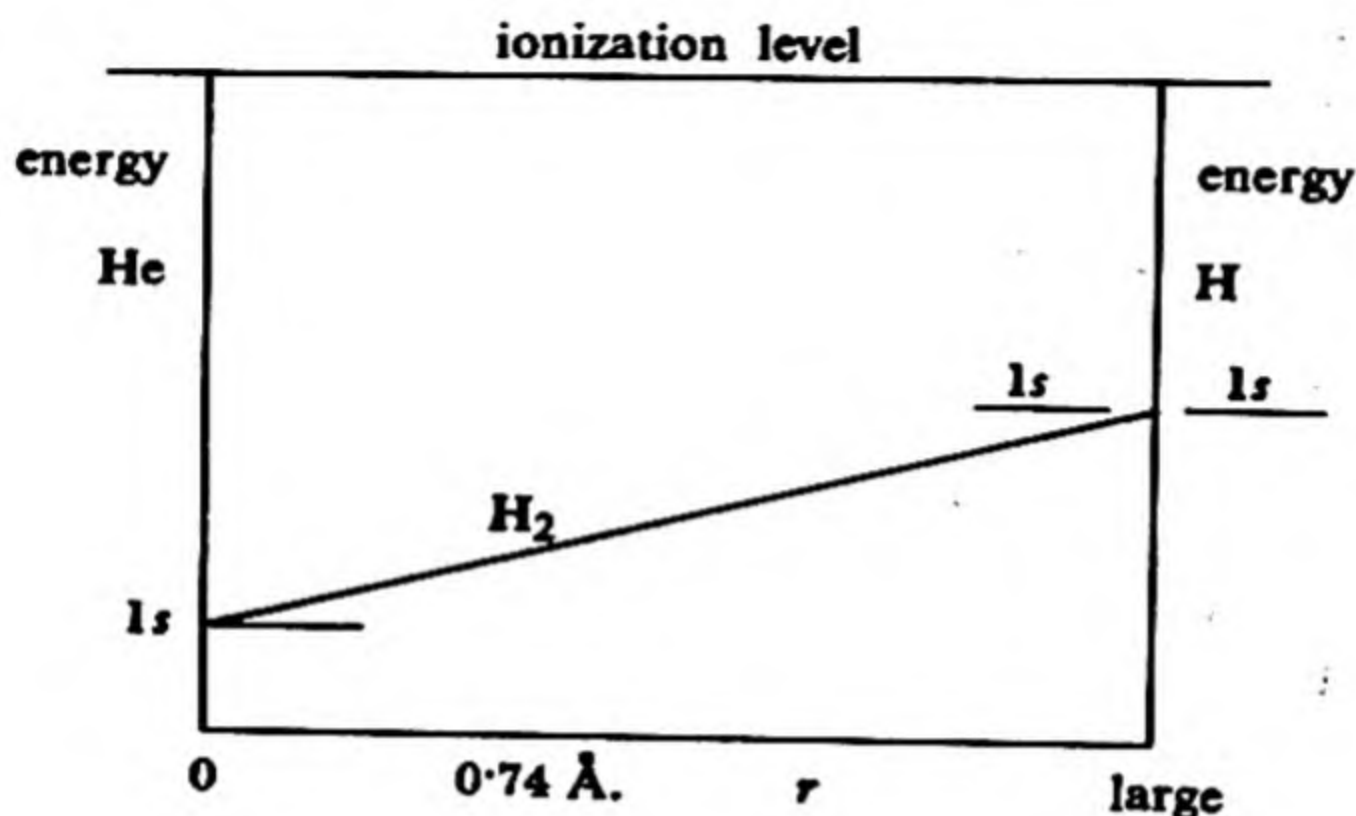


FIG. 30

We now suppose that the hydrogen atoms are brought increasingly close together until in the limit a 'fusion' of nuclei occurs, with the formation of a helium atom; or alternatively that a 'fission' of helium is possible, to yield two separate atoms of hydrogen. Such processes need no longer be rejected as imaginary. In either process the point must be reached at which the centres of hydrogen nuclei are separated by the distance 0.74 \AA , prescribing the hydrogen molecule. Now in a helium atom both electrons occupy the same (1s) orbital, and by the exclusion principle (p. 93) must have opposed spins; they must therefore also have opposed spins in the molecule and in the hydrogen atoms from which it can be formed.

The energies concerned in Fig. 30, being drawn from spectroscopic data, are solely *electronic* energies. As the atoms mutually approach, the attractive forces between an electron in one atom and the proton in the *other* steadily increase, and although repulsion

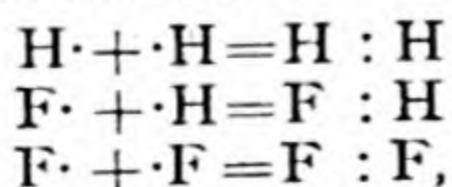
between electrons also increases, the diagram shows that the attractive forces prevail. The net electronic energy therefore falls continuously throughout the fusion process, which might seem to be a highly exothermic and spontaneous reaction. Fusion is indeed only prevented by one effect, of which the diagram takes no account: the *mutual repulsion of the protons*, that ultimately becomes overwhelmingly great. The mutual approach of the atoms is halted at a definite value of r (actually 0.74 Å.), where the protonic repulsion overtakes the net attractions between electrons and protons and the *total* energy begins to rise steeply. The molecule is stable because further compression is opposed by repulsive forces and separation of the atoms by attractive forces. The bond H—H thus originates from a balance of opposed forces: (1) protonic repulsion, (2) protonic bonding by the attraction of each electron.

Covalent and Ionic Bonds. It can truly be said, as the common chemical formulation $H : H$ suggests, that in molecular hydrogen the nuclei *share* the attraction of the electrons and that the bond results from a *co-operation* of all the charged particles in the original separate atoms. This type of bond is accordingly termed *covalent*. For an *ionic* bond (p. 103) electrostatic forces are no less responsible, but they result from a complete electronic transference to the electronegative atom. As the term 'electrovalent' can only mean 'bonding by electrical means' it is not distinctive, and should now be discarded.

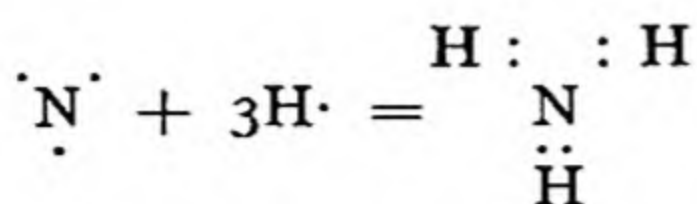
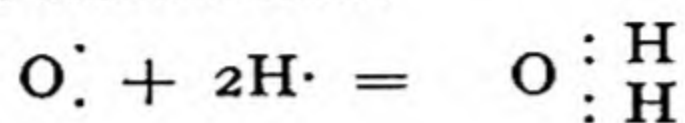
Valency and Electronic Configuration. Inspection of the chart of configurations on p. 94 discloses a striking fact: the number of singly occupied orbitals in the ground states of a majority of the atoms in Series 1 to 3 inclusive (hydrogen to argon) is numerically equal to their valencies towards hydrogen as established by chemical means (p. 74).

H	He	Li	N	O	F	Ne	
		Na	P	S	Cl	Ar	
I	0	I	3	2	I	0	Orbitals singly occupied
I	0	I	III	II	I	0	Valencies (to hydrogen)

This regularity can hardly fail to carry conviction that we may explain the formation, by covalent bonds, of such molecules as HF, HCl, F₂, and Cl₂ by substituting for one or both of the hydrogen atoms which form the molecule H₂, in the way already discussed, one or two atoms of fluorine or chlorine:



and the formation of water and ammonia by duplicating or tripling the electronic interactions:



The Valencies of Excited States. At the moment of its formation from atoms a molecule possesses all the energy of its formation, which is rapidly dispersed (necessarily in quanta) over atoms which have not yet entered into combination, some of which must thereby be raised into an excited state. These atoms on entering combination cause the excitation of further atoms, until ultimately all atoms will have reacted in an excited state. We must therefore examine how, if at all, their singly occupied orbitals are affected.

For atoms from beryllium to fluorine inclusive a state above the ground state and relatively near to it (Fig. 28) is arrived at by 'promoting' one of the paired 2s electrons to one of the vacancies in 2p orbitals.

	2s	2p _x	2p _y	2p _z	Valency
Beryllium	I	I	—	—	II
Boron	I	I	I	—	III
Carbon	I	I	I	I	IV
Nitrogen	I	2	I	I	III
Oxygen	I	2	2	I	II
Fluorine	I	2	2	2	I

Thus in beryllium, boron, and carbon singly occupied orbitals are increased by two, and their number now equals the established chemical valencies of these elements; in nitrogen, oxygen, and fluorine there is no alteration.

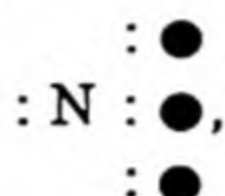
Hence the rule that *the valency of an element (to hydrogen) is numerically equal to the number of singly occupied orbitals in its electronic configuration* is quite general, if we remember to take into account the configuration of atomic states near in energy to the ground state. It is obvious that singly occupied orbitals are most likely to be found among the peripheral orbitals of an atom, which together compose the so-called 'valency zone.'

The Inert Elements. From the spectrum of helium we learn that to promote one of its two 1s electrons to the 2s orbital (and thus confer a possible bivalency, cf. beryllium) a quantum of about 20 electron-volts, i.e. 460 kcal. per gram-atom (p. 96) would be

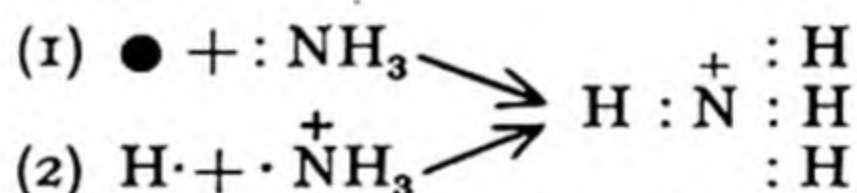
necessary. A quantum of such magnitude could not be provided by any conceivable chemical reaction into which the atom might enter. It is for such reasons that helium and the heavier inert elements maintain their resistance to chemical combination.

'Dative' Covalency—Co-ionic Bonds. It would appear that in the compounds hydrogen fluoride, HF, ammonia, NH_3 , and boron trifluoride, BF_3 , the respective valencies of the elements concerned are completely satisfied, or 'saturated.' Yet these gases all combine readily in pairs to give the stable compounds ammonium fluoride, NH_4F , fluoboric acid, HBF_4 , and amino-boron trifluoride, NH_3BF_3 .

In the electronic diagrams on p. 107 the symbol H really represents a proton. When this fact is emphasized by using the sign ● for a proton, ammonia would be written as

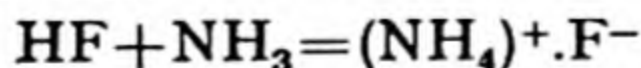


the diagram now including on the left the pair of 2s electrons already coupled in the nitrogen atom. The appearance of the structure suggests that a fourth proton is missing, and could be supplied if ammonia were in contact with a source of protons, i.e. an *acid*, as in (1) below:



The equivalent (but imaginary) reaction (2), in which a covalent bond is formed in the normal way by a contribution of one electron from each participant, demonstrates that in the ammonium ion $(\text{NH}_4)^+$ the nitrogen assumes a positive charge, and is covalently linked in an exactly equivalent way to each of the four hydrogen atoms. The hydrogen atom linked by process (2) becomes in the ammonium ion indistinguishable from the other three.

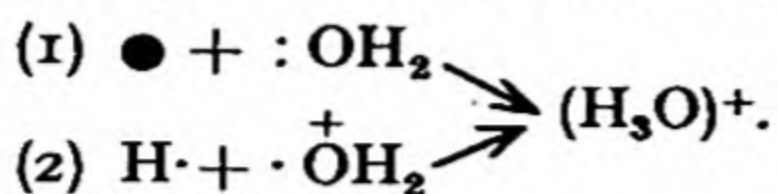
A glance at the chart on p. 94 indicates that an ion N^+ has the same electronic configuration as a carbon atom: N^+ and C are *isoelectronic* and must therefore possess the same *quadrivalency*. The question 'What is the valency of nitrogen in the ammonium ion?' does not arise, since the ion N^+ and not the atom is actually present. If the source of protons in reaction (1) above is hydrofluoric acid, the explanation of the reaction



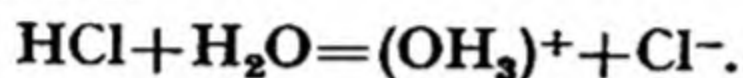
is now clear. Since in an ammonium ion all the five electrons in the valency zone of an element of atomic number 7 are fully used in

bonding, no further atom can be covalently bound. Ammonium fluoride and all the other ammonium compounds are necessarily ionic compounds, i.e. *salts*.

An entirely similar interaction occurs between a proton and *water*:

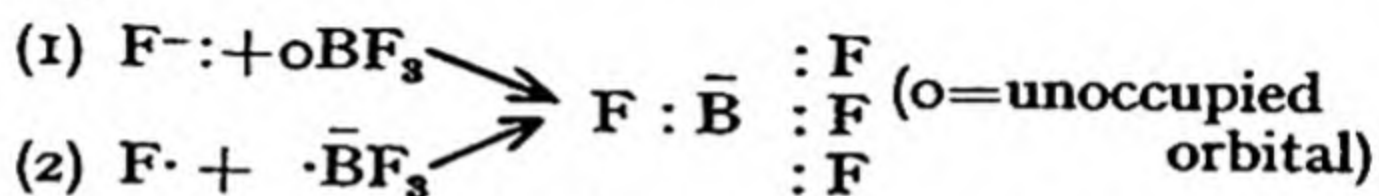


The result is the *hydroxonium* ion, commonly called 'hydrogen ion' in aqueous solutions. The ion O^+ , being isoelectronic with nitrogen, is tervalent. The conversion of hydrogen chloride, without acid properties, into hydrochloric acid when dissolved in water, is expressed in the equation:

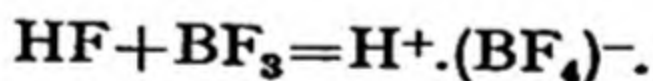


The close constitutional relation between NH_4^+ and CH_4 and between OH_3^+ and NH_3 extends to the spatial distribution of the bonds: in the former pair it is *tetrahedral*, and in the latter, *pyramidal*.

In a boron atom in the tervalent state (p. 107) one $2p$ orbital is still unoccupied. In the interaction of boron trifluoride with hydrofluoric acid it is the fluoride ion and not the proton which plays the active role:

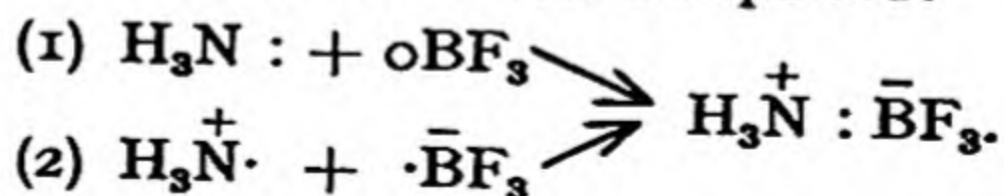


From these two alternative formulations we see the equivalence of all four fluorine atoms bound to the boron ion B^- , which like N^+ is isoelectronic with carbon, and the fluoborate ion BF_4^- is tetrahedral in shape. The full reaction with the acid is represented in the equation:



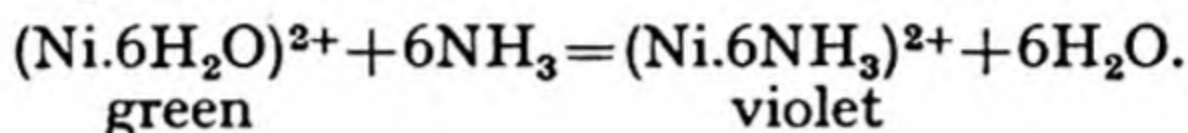
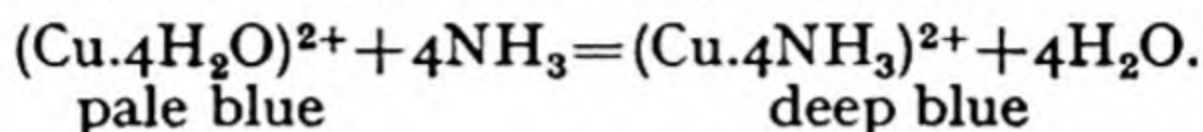
Since there is no possibility of linking the proton covalently with the anion, fluoboric acid is a strong electrolyte (p. 220).

The interaction of ammonia and boron trifluoride is in principle similar to that of fluoride with the latter compound:



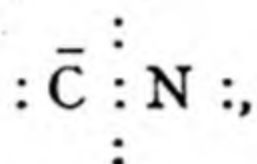
The product contains two *ions* bound by a *covalent* link, and may hence be termed *co-ionic*. The reality of the ionic charges is demonstrated by the fact that, while the isoelectronic $CH_3.CF_3$ is a gas, the ammino-boron trifluoride is a non-volatile crystalline solid, simulating a salt in this respect.

Complex Ions—‘Co-ordination Compounds.’ The power of such compounds as ammonia and water to form single covalent links for which the nitrogen and oxygen atoms respectively furnish both electrons is responsible for the existence of a very large range of complex cations and anions. The effect of adding aqueous ammonia to aqueous solutions of cupric or nickel salts (tests much used in qualitative analysis) is represented by the equations:



We deduce that in these examples, at least, the link $\text{H}_3\text{N}^+ : \text{Cu}^+$ is stronger than the corresponding link with water, probably because nitrogen is less electronegative than oxygen.

In the well-known ferrocyanides and ferricyanides, e.g. $\text{K}_4\text{Fe}(\text{CN})_6$ and $\text{K}_3\text{Fe}(\text{CN})_6$ cyanide ions,



are linked to a central iron cation Fe^{2+} or Fe^{3+} by the carbon atom. As the formulae demand, the net charge on the ferrocyanide anion is $2 - 6 = -4$, and on the ferricyanide $3 - 6 = -3$. Molecules or ions forming complex ions in this way are termed *ligands*. Complexes with uncharged ligands (NH_3 , H_2O , etc.) retain the charge associated with the simple ion, as in the copper and nickel complexes above.

Before the type of chemical bonding in such complex ions was elucidated it was customary to describe the linkages by the non-committal term ‘*co-ordination*’: this led to the naming of such a link, after the discovery of its nature, as a ‘*co-ordinate bond*,’ and alternatively as a ‘*dative covalency*.’ The sign $\text{A} \rightarrow \text{B}$ was often applied, A being termed the *donor*, and B the *acceptor*, atom. To-day it is probably preferable to use a description, such as *co-ionic*, which explicitly recognizes the link as a covalent bond

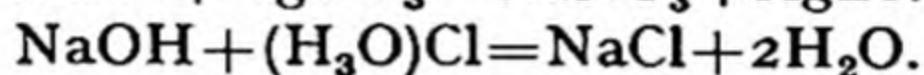
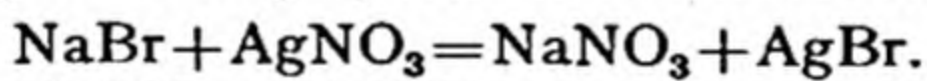
between *ions*, the sign being $\text{A}^+ - \text{B}^-$. The metals between scandium and copper inclusive in Series 4 of the Periodic System (often called *transition metals*) possess as many as nine orbitals ($4s$, $4p$, $3d$; see p. 93) in the peripheral or valency zone of their electronic arrangement, and it is obviously to these that we must principally look to provide cations with the six *vacant* orbitals required to produce a six-‘co-ordinated’ complex ion.

The Properties of Covalent and Ionic Compounds. The term *covalent compound* is used to mean a compound in which all bonds

are covalent. In an *ionic compound* of the binary type MX, e.g. NaCl, MgO, the bond is ionic, but, for example in sodium nitrate, calcium carbonate, calcium sulphate, or ammonium chloride, while there are ionic bonds $\text{Na}^+\cdot\text{NO}_3^-$, $\text{Ca}^{2+}\cdot\text{CO}_3^{2-}$, $\text{Ca}^{2+}\cdot\text{SO}_4^{2-}$ and $\text{NH}_4^+\cdot\text{Cl}^-$, within the compound ions the bonds are covalent. Hence most ionic compounds contain also covalent links.

As has been explained, all *ionic compounds* are, under normal conditions, solids with very strong binding between the constituent ions. They are thus non-volatile, often hard and brittle, and have high melting-points. Water exerts, however, a particularly powerful disrupting effect on many ionic crystals, which are therefore easily soluble in water (see Chapter XII): the solution, which contains the ions freed from the crystal, can undergo electrolysis. Only very few other liquids (sulphur dioxide, ammonia, hydrogen fluoride, hydrogen peroxide) exert a similar power on ionic compounds. Such compounds can also be electrolysed in the anhydrous fused state (e.g. Davy's discovery of the alkali metals), but a number of metallic compounds regarded as covalent at low temperatures (e.g. cuprous chloride, silver iodide) become ionized on melting.

Ionic compounds in general are thus likely to play the role of *electrolytes*. Reactions in solution between such compounds often proceed so rapidly that only special methods reveal their rates:



A *covalent compound* consists of *molecules* existing in all states, gaseous, liquid, and solid. Those that are under normal conditions liquids or solids have relatively low melting- and boiling-points. Since between covalent molecules there is only a small attraction, covalent compounds are miscible with or soluble in a large range of liquids. Water, however, which exerts so potent an effect on ionic compounds, is a poor solvent for the majority of such compounds; aqueous solutions when formed show commonly no better electrical conductivity than the solvent itself. Reactions between covalent compounds (as in the wide field of organic chemistry) proceed at only moderate and usually easily measurable rates (Chapter XIV).

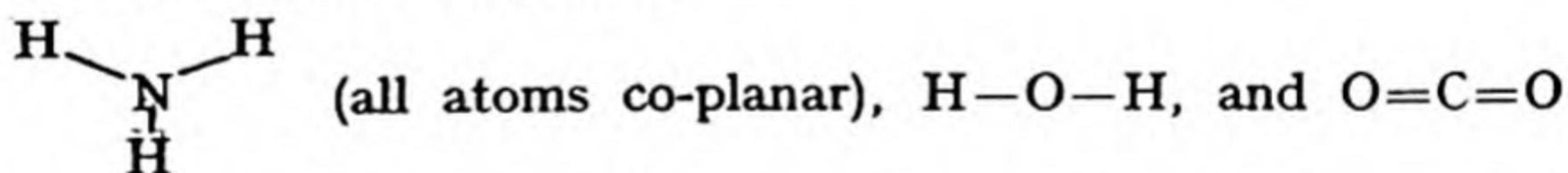
Polar Molecules. Amateurs of 'wireless' equipment will know that an electrical circuit containing capacity (condensers) and inductance (coiled wire) in parallel can be made to give rise, with the help of a thermionic valve, to oscillations of audio-frequency, with frequency proportional to the reciprocal of \sqrt{LC} , where L and C are the inductance and capacity respectively. Consider such a circuit with condenser of parallel plates so designed that it can be

evacuated or filled with various gases. With the inductance constant we observe the note of the audio-frequency. When the condenser contains the dry gases air, hydrogen, or carbon dioxide the note differs insensibly in tone from that given with the condenser evacuated: but with dry hydrogen chloride, dry ammonia, or water vapour in the condenser the note is flattened and therefore the frequency of oscillation reduced. The molecules of the second group of gases must therefore have some property, absent from those of the first group, which causes them to increase the capacity of the condenser. This can only be that of *electrical polarity*,

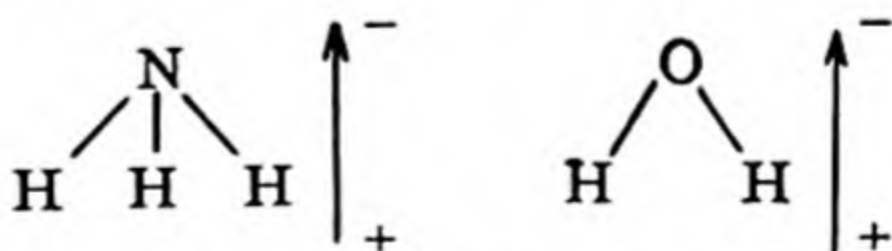
so that the molecules behave as rigid electric dipoles $\begin{smallmatrix} + \\ | \\ - \end{smallmatrix}$, and

align themselves in the electric field between the condenser plates, their positive ends towards the negative plate and conversely. The effect is equivalent to enlarging the plates and thus increasing the capacity.

One source of such polarity is easily seen. In the diatomic molecules H_2 , N_2 , and O_2 symmetry demands that the electrons functioning in their bonds should be equally shared between the atoms: but in a molecule such as HCl , wherein one atom is much more electronegative than the other, we should expect a definitely unequal sharing in favour of the halogen, necessarily conferring some dipolar character on the molecule. Nitrogen in ammonia, oxygen in water and carbon dioxide would be similarly favoured. Now if the spatial distribution of bonds in these gases gave to their molecules the bond diagrams:



(both linear) the individual dipoles would in such molecules exactly cancel each other, as our experiments show does happen in carbon dioxide (which is thus proved to be a linear molecule), but not in ammonia or water. Ammonia must therefore have a *pyramidal* diagram, with nitrogen above the hydrogen atoms, and that for water must be *triangular*.



Alignment of the polar molecules in the field of the condenser, being opposed by the random thermal motions, becomes less in degree with rise of temperature. The turning force producing

alignment is proportional to the *dipole moment*, $er = \mu$, where r is the distance between the charges e of the dipole. By means of apparatus of the type very briefly indicated above molecular dipole moments can be measured.

Molecule	$\mu \times 10^{18}$ (e.s.u. cm.)	$r \times 10^8$ (cm)	$e \times 10^{10}$	$\frac{e}{e}$
HCl	1.08	1.27	0.85	0.17
HBr	0.78	1.41	0.55	0.11
HI	0.38	1.61	0.23	0.05

In the table the first column gives the measured dipole moment of the hydrogen halides: the second the known distance between the nuclei of the atoms in the molecules. If it is assumed that the dipole charges are centred on the atoms the third column gives the dipole charges, and the last gives these charges expressed as a fraction of the full ionic charge ($e = 4.80 \times 10^{-10}$ e.s.u.).

Like most other natural phenomena chemical bonds refuse to be rigidly separated into categories, here the covalent and the ionic. Of each of these extreme types of bond we indeed recognize numerous examples, but most bonds between unlike atoms are of an intermediate character. We may predict that bonds between atoms of closely similar electronegativity will approach very nearly the extreme covalent type; and the extreme ionic type will be found between atoms differing greatly in electronegativity.

Electronegativity. In the changes (1) $\text{Cl} + e = \text{Cl}^-$ and (2) $\text{Cl}^+ + e = \text{Cl}$ energies equivalent to the electron affinity E and the ionization potential of chlorine I are released respectively. Hence in the change $\text{Cl}^+ + 2e = \text{Cl}^-$ the energy released is $I + E$. Since we may assume that Cl^- is electronically 'saturated,' with zero electron affinity, $(I + E)$ is the electron affinity (E.A.) of Cl^+ .

The scheme

0	$\text{Cl}^- :$	Cl^+	$I + E$
$\frac{I + E}{2}$	$\text{Cl} \quad :$	Cl	$\frac{I + E}{2}$
$I + E$	$\text{Cl}^+ \quad :$	Cl^-	0
E.A.			E.A.

in which the central member is the actual molecule Cl_2 , necessarily with an equally shared electron pair, shows the changes of electron affinity during a transference of the electron pair from right to left. From this it appears that the electron affinity of a chlorine atom in the molecule Cl_2 is measured by $\frac{(I_{\text{Cl}} + E_{\text{Cl}})}{2}$. The electron affinity

of a combined atom is known as its *electronegativity*, and gives a measure of the attraction of an atom for the electrons bonding it. The polarity of a molecule AB is directly dependent on the difference in electronegativity between A and B.

			H 56				
Li	Be	B		C	N	O	F
23	37	49		64	70	85	100
Na				Si	P	S	Cl
20				45	53	62	77

The table shows such electronegativities calculated as $\frac{(I+E)}{2}$, arbitrarily scaled to 100 for the most electronegative element fluorine. From the table we see that bonds C—H, B—H, C—N will approach the extreme covalent limit, while NaF, Li₂O, etc., will be ionic: bonds C—O, C—F, C—Cl, B—O, B—F will be of intermediate polar type.

Graphic, or Structural, Formulae. The first chemist to urge successfully upon his contemporaries the usefulness and significance of the symbol A—B for a (single) bond between atoms A and B, and to construct by its means such *graphic formulae* as we still use to-day, was ALEXANDER CRUM BROWN (1838–1922), who was Professor of Chemistry at Edinburgh, 1869–1908. Originally (1861) such formulae merely indicated a saturation of valency: thus bivalent oxygen was written —O—, hydrogen as H—, and water H—O—H. The joining of the valency dashes into a single stroke (1864) was much more than a mere convenience: it implied the then unknown mechanism by which the valencies became saturated, that is, forces between atoms. The force could hardly be the same in C—D as in A—B, although the same symbol was used in both cases. To-day we can be rather more explicit and replace the stroke by a colon sign (:) for a pair of electrons shared, but not necessarily equally, between the bound atoms.

Bond-Length. We have already used the notion of *bond-length* in obtaining atomic radii (p. 53), which were taken as half the bond-length A—A. It is an important question whether we can predict bond-lengths A—B as a sum of atomic radii, i.e. as

$$\frac{(A-A)}{2} + \frac{(B-B)}{2} = (A-B).$$

Since in the molecules from which we obtain the atomic radii the bonding electrons must by symmetry be equally shared, we may expect a predicted length to be close to that actually found

only when the atoms A and B have similar electronegativities. Taking atomic radii from p. 53 we find:

	<i>Bond-length (Å)</i>			<i>Difference in Electronegativity (p. 114)</i>
	<i>Predicted</i>	<i>Observed</i>	<i>Error</i>	
C—H	1.14	1.09	+0.05	8
N—H	1.11	1.02	+0.09	14
O—H	1.10	0.96	+0.14	29
C—N	1.51	1.47	+0.04	6
C—O	1.50	1.42	+0.08	21

A glance at Fig. 30 on p. 105 shows that the nearer the atomic nuclei can approach each other, i.e. *the shorter the bond-length, the stronger the bond*. We may therefore deduce from the above data that unequal electron sharing tends to strengthen a bond.

Stability of Bonds—Bond Energies. In recent years much information has accumulated, mainly from spectroscopic studies, upon the heats of dissociation of elementary molecules into their constituent atoms (*atomization*).

Heats of dissociation of diatomic molecules
(Kcal. per gm.-mol. of the gaseous element
at 25° and 1 atmosphere pressure)

H ₂ =2H,	104	Cl ₂ =2Cl,	58
O ₂ =2O,	118	Br ₂ (g)=2Br,	46
N ₂ =2N,	225	I ₂ (g)=2I,	36

Since these quantities of energy suffice to break the bonds between the atoms they may fairly be interpreted as *bond dissociation energies* (often shortened to *bond energies*). Given their heats of formation and the above heats of dissociation the bond dissociation energies of a range of other molecules can be calculated:

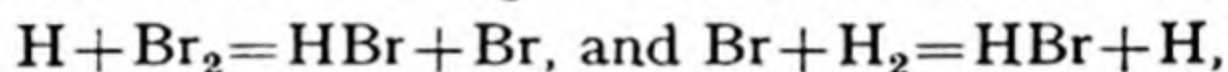
HCl	= $\frac{1}{2}$ H ₂ + $\frac{1}{2}$ Cl ₂ = H + Cl		
	22 52 29	Bond energy	103 kcal.
H ₂ O(g)	= H ₂ + $\frac{1}{2}$ O ₂ = 2H + O		
	58 104 59	" "	221 kcal.
NH ₃	= $\frac{1}{2}$ N ₂ + $\frac{3}{2}$ H ₂ = N + 3H		
	11 112 156	" "	279 kcal.
Cl ₂ O	= Cl ₂ + $\frac{1}{2}$ O ₂ = 2Cl + O		
	-18 58 59	" "	99 kcal.
O ₃	= $\frac{3}{2}$ O ₂ = 3O		
	-34 177	" "	143 kcal.

It should be noted that chlorine monoxide and ozone, which are endothermic compounds when formed from elementary *molecules*, become strongly exothermic when formed from *atoms*. In a table of heats of formation from atoms there are no endothermic entries.

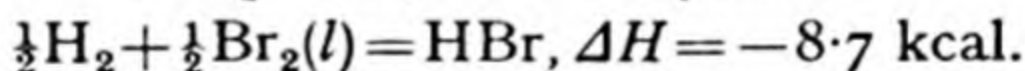
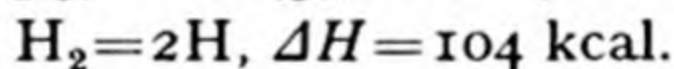
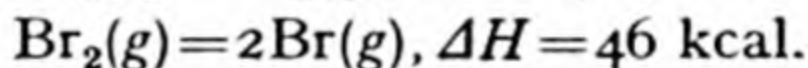
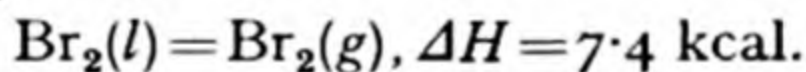
We are led to conceive that a chemical reaction, in which the atoms of reactants are rearranged into product molecules, consists essentially of two stages, (a) the rupture of bonds in the reactants, (b) the formation of new bonds in the products, and conventional heats of reaction are differences between the always *endothermic* process (a) and the always *exothermic* process (b). Although in an actual chemical change these stages overlap (p. 177), so that at no point in its course are free atoms present, Hess's Law assures us that for purposes of calculation we may assume that the reactants are completely 'atomized' and the atoms so obtained then reunited to give products.

A knowledge of directly determined heats of formation and heats of atomization may be used to predict heats of reaction which could not easily be directly observed; for example:

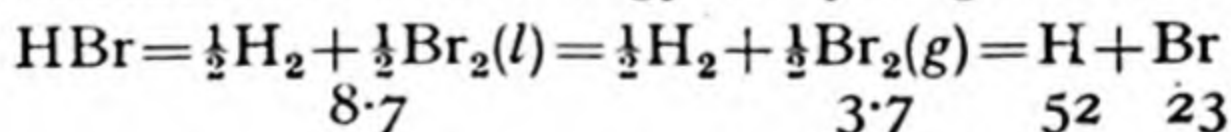
Calculate the heats of the gaseous reactions



given the following data:



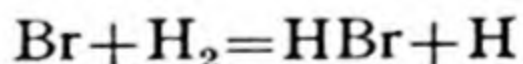
We first calculate the bond energy of hydrogen bromide:



Total for bond energy 87.4 kcal.

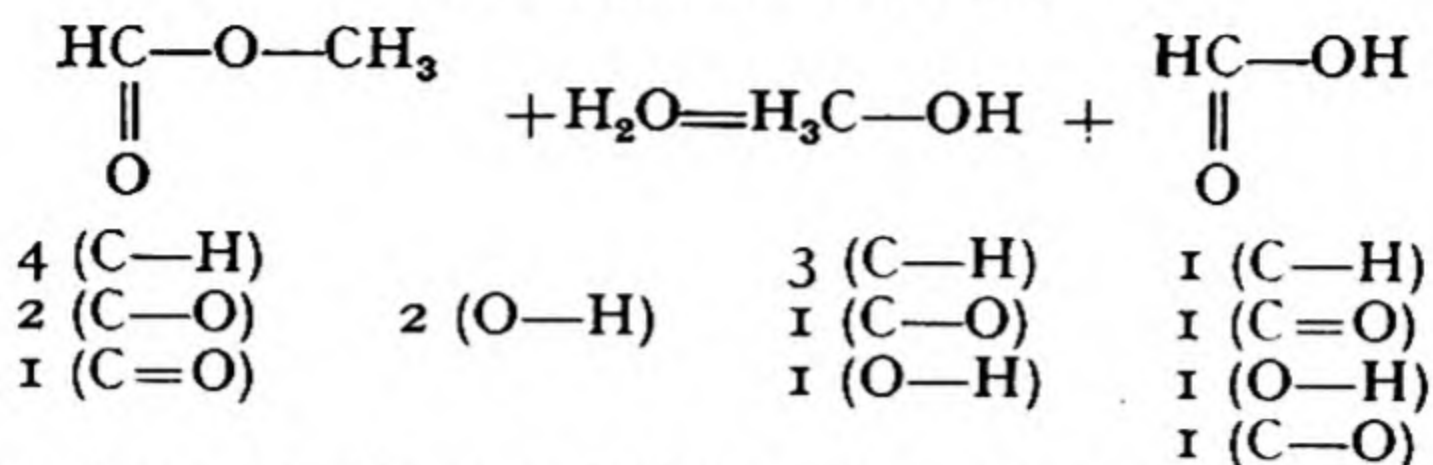
Then we have: $\text{H} + \text{Br}_2 = \text{HBr} + \text{Br}$

$$\begin{array}{rcl} 46 & -87.4 & \text{for bonds broken or made;} \\ \Delta H = 46 - 87.4 = & \underline{-41.4} & \text{kcal.} \end{array}$$



$$\begin{array}{rcl} 104 & -87.4 & \text{for bonds broken or made;} \\ \Delta H = 104 - 87.4 = & \underline{+16.6} & \text{kcal.} \end{array}$$

Many reactions between carbon compounds described in organic chemistry take place with very small heat change: the hydrolysis of methyl formate (cf. p. 174) can be described as *thermo-neutral*, since practically no heat is released or absorbed.



It is seen from the above tabulation that there is an equal number of the same types of bond on each side of the equation.

Multiple Bonds. Although logically sanctioned by the principle of valency saturation in chemical compounds, the *multiple bond*, in which two atoms mutually saturate more than one unit of their combining powers, gained recognition rather slowly. Impetus towards its acceptance was given by the success of Kekulé's scheme, proposed in 1865, for the bonding in the hydrocarbon, benzene (C_6H_6). In his formula the quadrivalency of carbon was maintained by supposing the six carbon atoms to be arranged in a ring, in which each atom was linked to one of its neighbours by a 'double' bond, symbolized by $\text{C}=\text{C}$. The great stability and chemical inertia of the nitrogen molecule N_2 makes it difficult to believe that the tervalency of each atom is not completely satisfied, here necessarily in a 'triple' bond.

To-day we recognize that in their short length lies one of the most certain criteria for discriminating multiple bonds.

Lengths of Multiple Bonds (Å.)

Triple	$\text{N}\equiv\text{N}$	$\text{HC}\equiv\text{N}$
	1.09	1.15
	(1.48)	(1.47)
Double	$\text{H}_2\text{C}=\text{O}$	$\text{H}_2\text{C}=\text{CH}_2$
	1.20	1.33
	(1.42)	(1.54)

We see that double bonds are about 14 per cent and triple bonds about 25 per cent shorter than the corresponding single bonds (given in parentheses).

As has been explained in the previous section, methods are now available for determining the *bond dissociation energies* needed to rupture specific chemical bonds. For the bonds listed above and the corresponding single bonds these energies are as follows:

Bond-Dissociation Energies (kcal.)

$\text{C}-\text{N}$	$\text{C}\equiv\text{N}$	$\text{C}-\text{C}$	$\text{C}=\text{C}$
69	214	83	146
$\text{C}-\text{O}$	$\text{C}=\text{O}$		
82	174		

These data give much support to the rule previously mentioned—*the shorter the bond, the greater its strength.*

Hydrogen Bonds. While ammonia, water, and hydrogen fluoride, being volatile, are to be classed as covalent compounds, their boiling-points are abnormally high when compared with their immediate analogues of higher molecular weight:

NH ₃	−33°	H ₂ O	100°	HF	19°
PH ₃	−85°	H ₂ S	−62°	HCl	−83°

Water, which shows the greatest anomaly in boiling-point, has other unusual properties:

- (1) The molar latent heats of fusion and evaporation are very large; 1.44 kcal. and 9.7 kcal, respectively; compare methane, 0.22 and 2.0 kcal.
- (2) Ice is less dense (0.916 gm./c.c.) than water at the freezing-point.
- (3) The temperature of the maximum density of water is not its freezing-point but 4° higher (deuterium oxide, 'heavy water,' has F.P. 3.8° and maximum density at 11.2°).

It is no accident that life on the earth is conditioned by these properties. Fresh water can be retained in natural or artificial reservoirs in spite of annual or secular rise of temperature (1). During cold periods such stores of liquid water are protected from complete solidification (2, 3). Water at its freezing-point, being less dense than at 4°, remains at the surface and there forms a layer of ice with very poor heat conductivity and largely protecting the liquid below at 4° from further cooling. The benefit of such natural protection of water supplies is only very slightly offset by the common need for a plumber's visit after periods of frost.

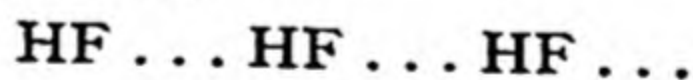
The presence of even small amounts of dissolved salts lowers the temperature of maximum density: sea-water increases in density down to its freezing-point (about −2.3° for oceanic water), but much protection from freezing in depth is gained from the large heat of fusion (1). The cooling and preservation of water in hot climates by storing it in porous earthenware vessels were known in antiquity.

In most crystalline solids composed of molecules the latter are packed as closely as their shapes permit. When the crystal units are spherical (inert gases or metals) each is in contact with twelve others; in the terminology of crystal physics such packing is called '12-co-ordination' or 'close-packing.' Since a proton is immensely smaller than an atom, simple covalent hydrides such as CH₄, NH₃, H₂O, or HCl have nearly spherical molecules (the diagrams drawn in this and other text-books to explain the bonding in such molecules are very deceptive in regard to their actual shape). Accord-

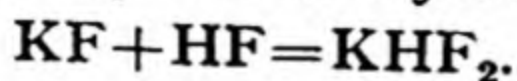
ingly crystalline methane or hydrogen chloride contain very nearly close-packed molecules (with 12-co-ordination). On the contrary, in ice (one of the first crystals to be examined by X-ray diffraction) each molecule H_2O is surrounded by no more than *four* others placed at the corners of a tetrahedron in which the first molecule is inscribed. The centres of molecules are found to be 2.76 Å. apart. Spheres of this diameter, each of mass $18/N$ (N = Avogadro number), when close-packed would yield a solid of density 2.0 gm./cm.³.

Therefore in ice there must exist some factor sufficiently powerful to prevent close-packing, and explain the very open, lace-like structure, in agreement with its low density. We have seen that in the water molecule the electronegative oxygen draws towards itself the bonding electrons, leaving the proton charges exposed at points on the surface of the molecule separated by about the 'tetrahedral angle,' 108° . The table on p. 94 shows that, in addition to the two electrons contributing to the OH links, oxygen has two (non-bonding) electron pairs. We have only to assume that these negative charges are localized at the two points of a tetrahedron not already occupied by protons to explain the constitution of ice. The electrostatic attraction between the positive proton centres in one molecule for the negative centres in another gives just the packing actually found. Hydrogen, being already 'saturated' electronically by its union in a water molecule, cannot share further electrons. The so-called 'hydrogen bond' linking molecules in ice thus simulates an ionic bond; its bond dissociation energy is estimated as about 6 kcal.

On melting, some of the hydrogen bonds in ice are broken (hence the high latent heat), and the water molecules released become more closely packed: the density rises. At 4° , the temperature of maximum density, the thermal expansion of the water has just equalled the contraction so brought about, but even at the boiling-point about 40 per cent of the bonds still exist. Their final rupture accounts for the high latent heat of evaporation. Of the hydrides NH_3 , H_2O , and HF only water has the correct number of hydrogen atoms to produce the full three-dimensional bonding present in ice. Hydrogen bonds persist even in gaseous hydrogen fluoride, but they can only give rise to *chains*:



Alkali-metal fluorides readily absorb hydrogen fluoride:



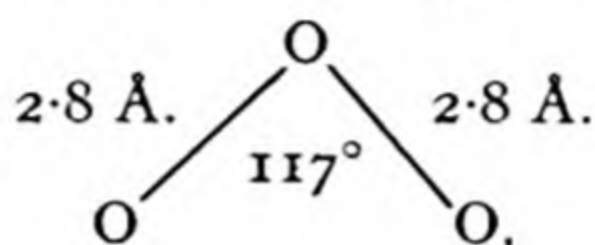
The product KHF_2 contains the anion $\bar{\text{F}}.\overset{+}{\text{H}}.\bar{\text{F}}$ in which the bonds are probably fully ionic, and so strong that the anion continues to exist when the 'difluorides' are dissolved in water.

Delocalization of Electrons. In all examples discussed so far we have presumed that bonding electrons exert their powers on two atoms only; we may say they are *localized* between two atoms. From the facts about the molecular structures of many compounds, however, we are compelled to infer a wider scope of bonding power.

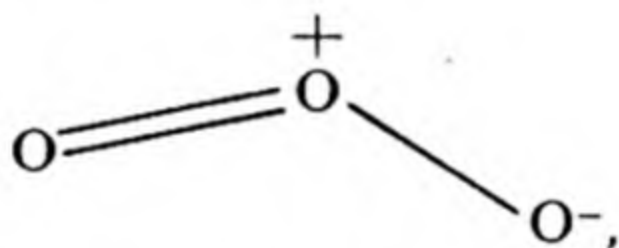
The graphic formula of ozone, O_3 , was for long assumed to be



with an atom at each corner of an equilateral triangle, but examination by modern methods (mainly electron diffraction) proves its structure to be represented by the diagram

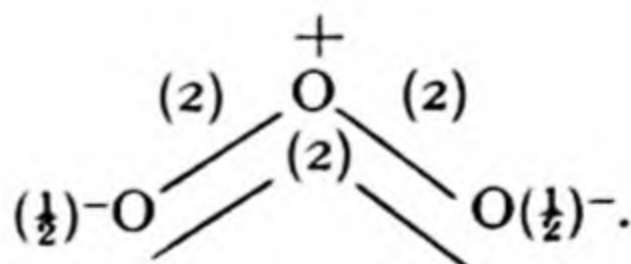


that is by an isosceles triangle. A molecule O_3 can be built by assuming a co-ionic bond between one atom of a molecule O_2 and a third oxygen:

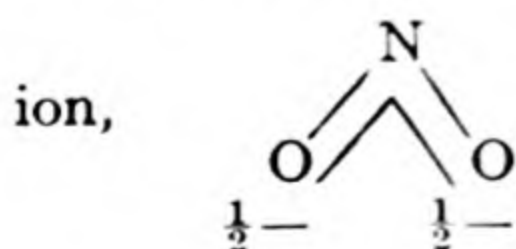


but since the double bond will be shorter than the single the shape of such a molecule is a *scalene* triangle.

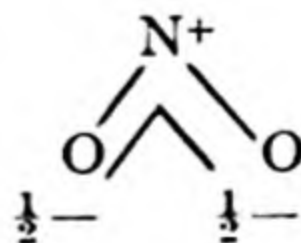
There is only one way to secure the symmetry of the actual molecule and that is to make the two bonds alike, by assigning to one of the electron pairs in the double bond the role of binding equally all *three* atoms, thus:



Further examples of an electron pair binding three atoms in simple structures are to be found in nitrous oxide, $\overset{+}{N}=\overset{-}{N}-\overset{-}{O}$, nitrite



, and the nitro group, $\begin{array}{c} N^+ \\ \diagup \quad \diagdown \\ O \quad O \\ \frac{1}{2}- \quad \frac{1}{2}- \end{array}$



The Metallic Bond. The metals provide the most extreme examples of delocalization. In sodium, as in the majority of metals, the atoms are densely packed, and any one atom is symmetrically surrounded by eight others, all in contact with it. Now a sodium atom, like that of hydrogen, possesses only one 'valency' electron, and, assuming localized electrons, it could be linked to no more than one other atom, in a molecule Na_2 . The structure of the metal is, however, a packing of *atoms* and not molecules, and its only possible interpretation is a *complete* delocalization in which n electrons exert combining power over n atoms equally, where n may be indefinitely large.

Electricity is conducted through material substances in two ways—(a) the *electrolytic*, by the movement of charged *ions*, as in the conduction by fused salts or salt solutions; (b) the *electronic*, by the movement solely of *electrons*, as in metallic conductors. It can be shown that electronic conduction is a necessary consequence of the electronic delocalization described above.

Typical Non-metallic Structures. (a) *Carbon.* In diamond every carbon atom is directly linked by a single localized electron-pair bond to each of *four* others, which surround it tetrahedrally. As in a metal, the packing in the crystal is of atoms and not molecules; in both cases the structure is termed *macromolecular*. In such a structure no closed surface can be constructed within the crystal through which chemical bonds do not pass. The physical properties of diamond are, however, in the strongest contrast with those of a metal: it is very hard, brittle, transparent, and an insulator.

(b) *Phosphorus.* The 'white' allotrope consists of discrete molecules P_4 , in which each atom is situated at a corner of a regular tetrahedron of atoms, and is thus linked to *three* others. In its low melting-point and volatility 'molecular' phosphorus is contrasted with the macromolecular diamond.

(c) *Sulphur.* The characteristic unit of the solid is a molecule S_8 in the form of a ring in which each atom is linked by single bonds to *two* others. Since the directions of the two bonds are not collinear the ring is necessarily 'crumpled' (Fig. 95, p. 518).

(d) *Iodine.* The atoms are linked in *pairs*, and the packing of the crystal is of diatomic molecules I_2 .

In these examples the numbers of nearest neighbours to any atom are respectively 4, 3, 2, and 1, which strictly accord with their valencies. On the contrary valency plays only a subsidiary part in the metallic structure.

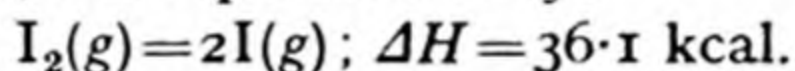
CHAPTER XI

CHEMICAL ENERGY (II): THE CONCEPT OF FREE ENERGY: CHEMICAL EQUILIBRIUM

Introductory. By means of X-ray diffraction the detailed structure of crystalline iodine has been revealed as consisting of molecules I_2 which, at low temperature, are sited at fixed positions in a regular 'lattice.' In every part of a crystal the molecules surrounding any one other are situated in precisely similar positions in respect to it. In the molecules the atoms are bound with a constant distance (2.70×10^{-8} cm.) between their centres. Thus the units composing the crystal are in *perfect order*, and no latitude is allowed in their placing. In a crystal at normal or higher temperature this strict order is slightly blemished, owing to the small thermal vibrations of the molecules and atoms round their still fixed points of anchorage. When brought into a heated container crystals of iodine volatilize spontaneously:



At high temperature (700°C.) atomization of the molecules of the vapour takes place, also spontaneously:



Since no bonds exist between molecules in the state $I_2(g)$, nor between atoms in the state $I(g)$ these positive heats of reaction are respectively the energies per mole binding molecules in the crystal, and binding atoms in the molecule. As we should expect, the second is the larger. There is clearly a decrease of chemical stability in each reaction, for no new bonds replace those broken. It is plain even from these very simple examples that increase of total chemical stability cannot be the *sole* 'driving force' of spontaneous reactions (cf. Chapter VII, p. 73).

Change of Order into Disorder. The tendency of order to be replaced irreversibly by disorder is exemplified by many common occurrences. When a maximum degree of randomness has been introduced into a new pack of playing cards by shuffling we feel intuitively quite sure that the chance of the original order being restored by further shuffling is extremely minute (although not *infinitely* small). A manufacturer of tennis balls for export, intending to economize in packing materials, instructs his staff to pack the balls tightly in a perfectly orderly way, one ball above another in regular columns. Soon discovering that wages paid for time so

spent much outweigh the saving in packing-crates, he contents himself with allowing the balls to be tumbled at random into their receptacles, perhaps ruefully reflecting that the chance of any crate so filled proving to contain balls in perfect order, and therefore a maximum number, is utterly negligible. From the first example and many others like it we deduce that restoration of order by the continued agency of the process which has produced disorder is nearly (but not quite) impossible: from the second that a disordered assembly has a much greater *probability* than an ordered one.

Turning back to the example of the previous section we notice that in the volatilization of iodine the order in the setting of molecules in the crystal is completely lost: but the order within the molecules survives; in atomization the latter also disappears, and a final state of disorder is reached. We seem compelled to postulate that it is the increase of *probability* (or randomness) that successfully competes with the adverse decrease of chemical stability in causing the changes described.

Organized and Disorganized Energy. While a billiard ball is falling on to a marble floor all its molecules possess parallel components of downward velocity equal to that of the ball; the corresponding kinetic energy of the molecules is fully *organized*. Collision with the floor, which may be regarded as perfectly elastic, exactly reverses the parallel molecular velocities and therefore does not detract from the organization of the kinetic energy. The ball rises again to its former height, performing *work* against the force of gravitation, which exactly consumes the kinetic energy acquired in the fall. A ball of putty of equal mass falling in the same circumstances has the same organized kinetic energy when it hits the floor, but in that inelastic encounter the equal parallel velocities are converted into a wide range of velocities in random directions. The organized energy gained in the fall is dissipated as (disorganized) *heat energy*, and the ball, although still possessing as heat all the necessary energy, does not rise from the floor.

Free Energy. Organized energy is called *free energy* (symbol G) because under suitable conditions it is freely, i.e. quantitatively, interconvertible with *work*. During its fall the billiard ball receives an increase of free energy ΔG because gravitational force does work w upon it; in its rise the free energy so gained is reconverted into work, since the ball then does work w against the force of gravitation. Hence in this case — $\Delta G = w$.

Reversibility and Irreversibility. The example of the ball of putty shows that it must not be supposed that a gain of free energy *necessarily* entails an output of an equivalent amount of work. Both putty and the billiard ball receive equal increments of free energy ΔG in their fall, but their subsequent behaviour differs

because of the unlike nature of their collision with the floor. The one is a *perfectly reversible* process (all downward parallel molecular velocities reversed in direction) and the other completely *irreversible* (parallel velocities converted into velocities in random directions). A ball of many other materials would rebound after collision with the floor, but not regain its original height; in such cases the collision is *partially* reversible.

These simple examples illustrate the fact that in the relation $-\Delta G = w$, the second term is the *maximum* work, obtainable only under conditions of perfect reversibility. For a fixed decrement $-\Delta G$ the work obtained can vary from zero to this maximum, depending on whether the conditions admit only of irreversibility, of partial reversibility, or ideal reversibility. Determinations of heat of reaction ΔH in a calorimeter are examples of chemical change carried out under completely *irreversible* conditions, when the sum total of energy changes is released as heat. Electrical methods of carrying out reactions under completely *reversible* conditions are described in Chapter XVIII.

Entropy. It has been found possible to establish a measure of the degree of probability, randomness, or disorder in an assembly of chemical units. This measure is a quantity termed *entropy*,* generally given the symbol S . The main importance of this quantity in chemistry lies in the fact that the product *absolute temperature* \times *entropy* (TS) affords a measure of the *disorganized* energy of the assembly. If a system undergoes a chemical change at constant temperature T and at constant pressure the change of disorganized energy is $T(S_2 - S_1) = T\Delta S$, where S_1 and S_2 are respectively the total entropy of the reactants and of the products. The parallel change of *total* energy is the change of enthalpy $H_2 - H_1 = \Delta H$. The change in organized or free energy $G_2 - G_1 = \Delta G$ must therefore be:

$$\Delta H - T\Delta S = \Delta G.$$

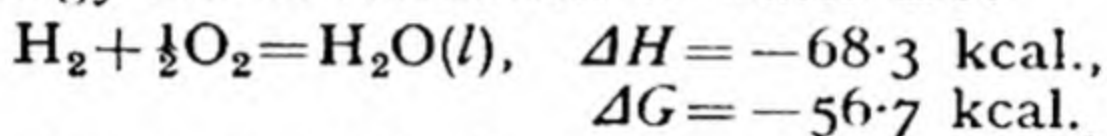
As assumed in the above derivation of this equation the change of free energy ΔG and the change of entropy ΔS both obey a law similar to that of Hess for ΔH and ΔU (p. 70) in being *independent of the path of a change*.

The 'Affinity' of Chemical Reactions. In the left-hand member of the above equation account is taken of the *two* factors which we have recognized as giving a 'spur' or 'driving force' to a chemical change: ΔH , a quantity which by its *decrease* measures the greater stability of the products over that of the reactants; ΔS , which by its *increase* measures the increase of disorder or randomness. The

* The term *entropy* was introduced about 1845 by the German physicist CLAUSIUS, who apparently derived it from the similar Greek word *entropē*, but a relation in meaning is obscure.

joint effect of the factors is subsumed in the single right-hand member of the equation, ΔG , the change of *free energy*. We can express concisely the law of chemical change: *a chemical change can proceed spontaneously* (at constant temperature and pressure) *only when it entails a decrease of free energy* (i.e. negative ΔG). In particular, spontaneous endothermic reactions (ΔH positive) must depend entirely upon increase of entropy for 'driving force.' The quest of the early chemists to gauge 'affinities' of reactions here reaches its final goal: chemical affinity is measured, not, as the French chemists supposed (p. 73), by the change of *enthalpy* ΔH , but by the change of *free energy* ΔG .

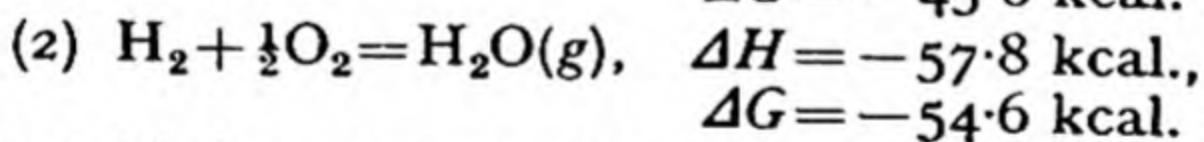
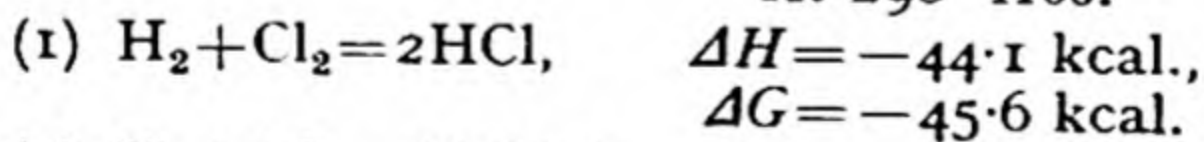
It will be noted that the law formulated above contains the permissive 'can proceed' rather than the compulsive 'will proceed.' At 25°, both gases being at 1 atmosphere pressure, the heat ΔH and the free energy ΔG of formation of water are:



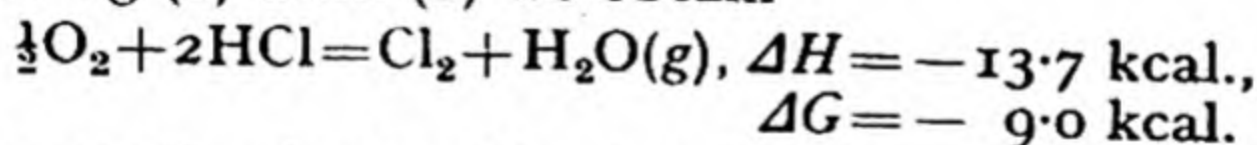
In spite of the large possible decrease of free energy concerned, hydrogen and oxygen each at 1 atmosphere pressure may be mixed at 25° without any chemical action being detectable. However, the result of exposing the gas mixture to a trace of finely divided platinum, or to an electric spark, demonstrates dramatically the large 'driving force' of the reaction. (Materials, such as platinum in this case, that can affect a chemical reaction in a way not unlike that of a lubricant upon machinery, are termed *catalysts*, and are further discussed in Chapter XV.)

Application of the Law of Chemical Change. As an illustration we consider whether it is possible on the large scale to recover chlorine from hydrogen chloride by direct air oxidation.

At 298° Abs.



On subtracting (1) from (2) we obtain



Hence this reaction is *possible* at 298° Abs., or 25° C., but is found to proceed at this temperature with such extreme slowness as to be undetectable (cf. hydrogen and oxygen, above).

The entropy change ΔS at 298° Abs. is easily calculated:

$$\Delta S = \frac{\Delta H - \Delta G}{T} = \frac{-13,700 + 9,000}{298} = \underline{\underline{-16 \text{ calories / deg.}}}$$

The entropy change, being negative, is unfavourable to the reaction desired, and rise of temperature, through the product $T\Delta S$, will increase its unfavourable influence. The answer to the problem is therefore that a profitable operation of the reaction is probable only if a catalyst can be found to hasten reaction at relatively low temperature.

The process flourishes to-day as the *Deacon process* (p. 543), cuprous chloride, CuCl , having proved a satisfactory catalyst.

The Molar Free Energy of an Ideal Gas. We must suppose that the free energy G possessed by a quantity of a substance under given pressure p and at temperature T forms a definite proportion of its total energy, and that this proportion changes with alteration of pressure and/or temperature. Without the introduction of any propositions other than those already outlined in previous sections it may be shown that for a small change of pressure dp at constant temperature T the resulting change in free energy dG is $dG_T = V dp$, V being the volume occupied by the substance. Therefore at constant temperature free energy increases with rise of pressure, and conversely.

For the particular case of a gram-molecule of a gas assumed to behave ideally, $V = \frac{RT}{p}$. Hence $dG_T = -\frac{RT \cdot dp}{p} = RT \cdot (d \log_e p)$. (It is a well-known mathematical fact that a small change dx in x causes a consequential change $\frac{dx}{x}$ in $\log_e x$.) When the pressure of a gram-molecule of the gas is changed from p_1 to p_2 at constant temperature T the change of free energy is therefore:

$$\Delta G_T = RT(\log_e p_2 - \log_e p_1).$$

If pressure is measured in atmospheres and $p_1 = 1$ atmosphere the change becomes:

$$\Delta G_T = RT \log_e p_2$$

(for logarithms to any base $\log 1 = 0$). Hence if the free energy possessed by one gram-molecule of the gas at 1 atmosphere and temperature T is G_0 , its free energy at pressure p is:

$$G_T = RT \log_e p + G_0.$$

How the *absolute* value of G_0 might be obtained is a difficult question, with which we shall not need to concern ourselves.

Chemical Equilibrium. A chemical reaction can continue spontaneously to a point beyond which the free energy can decrease no further. This terminal point may or may not coincide with effectively complete transformation of the reactants into the products: it is quite possible that the free energy may reach a minimum before reaction is complete. At such a point a state of *chemical equilibrium*

is set up, in which reactants and products remain together in definite proportions. The free energy runs 'downhill' to the same minimum point whether the reaction is started from 'reactants' (on the left-hand of the equation) or from 'products,' and we can logically no longer use such terms. Since its free energy has reached a minimum we see that *from a chemical system in equilibrium no work can be obtained*, even by a perfectly reversible process. This provides the most penetrating and satisfactory definition of such an equilibrium. Since free energy change ΔG must depend on temperature, principally through the term $T\Delta S$, it can be deduced that the position at which equilibrium is set up will vary with change of the temperature at which a reaction is conducted. To denote a state of equilibrium the sign \rightleftharpoons is used.

The Law of Mobile Equilibrium. To illustrate the proof of this most important law we take a very simple example of chemical equilibrium, a gaseous dissociation such as $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$, which we generalize in the expression $A \rightleftharpoons 2B$. In the discussion it will be assumed that the gases may be considered as ideal. A quantity of the gas A is placed in a vessel and kept at constant temperature T and pressure P until equilibrium is established between A and its dissociation product B . The partial pressures of the gases will then reach the constant values p_A and p_B ($p_A + p_B = P$).

Consider the situation just before equilibrium is reached, when the partial pressure of A is still slightly in excess of the equilibrium value, and a very small fraction x of a gram-molecule has still to dissociate, giving $2x$ gm.-mol. of B . Up to the attainment of equilibrium the *total* free energy of the system decreases, so that the decrease of molar free energy in the loss of A is greater than the gain in the formation of B : just beyond the equilibrium point the total free energy would begin to rise again. Consequently in the last small fractional change the competing changes of molar free energy exactly balance:

$$2x[RT \log_e p_B + (G_0)_B] = x[RT \log_e p_A + (G_0)_A] \quad (\text{p. 126})$$

$$\log_e \frac{p_B^2}{p_A} = \frac{(G_0)_A - 2(G_0)_B}{RT}$$

It will be recalled that G_0 was defined (p. 126) as the free energy per gram-molecule of gas at 1 atmosphere at a specified temperature T . Hence $2(G_0)_B - (G_0)_A$ is the free energy (change) ΔG of the reaction $A(g) = 2B(g)$ when carried to *completion* at temperature T .

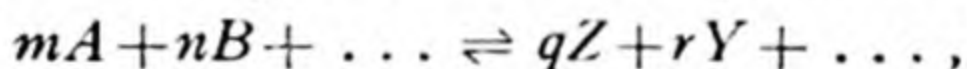
$$\text{Hence} \quad \log_e \frac{p_B^2}{p_A} = \frac{-\Delta G}{RT} = \text{a constant} = \log_e K_p \text{ say,}$$

$$\frac{p_B^2}{p_A} = K_p.$$

K_p is termed the *equilibrium constant* of the system $A \rightleftharpoons 2B$, and is independent of pressures, but changes its value with change of temperature T at which the equilibrium is established. The function of partial pressures on the left hand may be termed the *equilibrium quotient*.

Suppose that after equilibrium has been established between A and B at temperature T and in a vessel of volume V the gaseous mixture was compressed to volume $\frac{V}{2}$ without allowing a change of temperature. If the position of the equilibrium were unaltered the partial pressures must rise to $2p_A$ and $2p_B$ and the equilibrium quotient to $2 \frac{p_B^2}{p_A} = 2K_p$. Hence the effect of the compression is to cause the point of equilibrium to shift towards greater pressure of A and a consequent lesser pressure of B until the quotient is restored to its value K_p . In short, compression causes a diminution in the extent of the dissociation of A (see also p. 132).

Generalization. Although a simple example of chemical equilibrium was chosen in the previous section, the reasoning can obviously be extended without any change of method to include gaseous systems of many constituents expressible as follows:



for which the equilibrium quotient is:

$$\frac{p_Z^q \cdot p_Y^r \cdot \dots}{p_A^m \cdot p_B^n \cdot \dots} = K_p.$$

The spontaneous shift of the position of equilibrium required to maintain the constancy of the equilibrium quotient explains and justifies the title 'the law of *mobile* equilibrium,' which is however still often cited as the 'law of mass action,' a description both vague and ambiguous, since it is also used to embrace certain rules concerning *rates* of chemical action (Chapter XIV).

To apply the law of mobile equilibrium the only requisite is a chemical equation; no further information, on the chemical paths by which the state of equilibrium is reached, nor on the rates of progress along them, is needed. Conversely the results of such application cannot inform us on the mode or rate of reaching equilibrium but only of its final position. We have here an example of a general characteristic of the results of reasoning based upon energy changes obeying a law similar to that of Hess (p. 124); they can tell us whether change is possible, and if so in what direction it will occur, but upon all *rates* of reaction and the corresponding chemical mechanisms there is silence.

Extension of the Law to Solutions. The *molar concentration* C_A , conveniently expressed in the form $[A]$, is defined as the amount of A in gram-molecules contained in one litre. For n gm.-mol. of an ideal gas $p = \left(\frac{n}{V}\right) \cdot RT = C_{gas} \cdot RT$. Hence we can express the equilibrium quotient in the alternative form:

$$\frac{[Z]^q, [Y]^r \dots}{[A]^m, [B]^n \dots} = K_p (RT)^b = K_c,$$

where $b = (q + r + \dots) - (n + m + \dots)$; similarly to K_p , the alternative constant K_c is independent of concentrations, but alters with change of temperature.

Remembering that the behaviour of gases more closely approaches the ideal the lower the pressure (or concentration), we may expect by analogy that an equilibrium set up between substances in *dilute* solution will conform to this relation, and a very large number of experiments confirms this prediction.

Solids in Chemical Equilibria. Solids frequently take part with gaseous reagents in establishing equilibria; simple and well-known examples are:

- (1) $\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$,
- (2) $\text{NH}_4\text{Cl} \rightleftharpoons \text{NH}_3 + \text{HCl}$,
- (3) $4\text{H}_2\text{O} + 3\text{Fe} \rightleftharpoons \text{Fe}_3\text{O}_4 + 4\text{H}_2$.

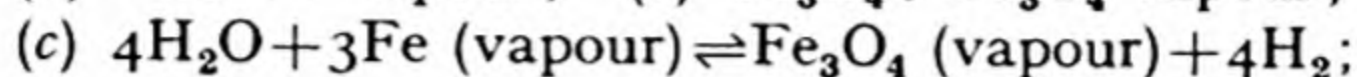
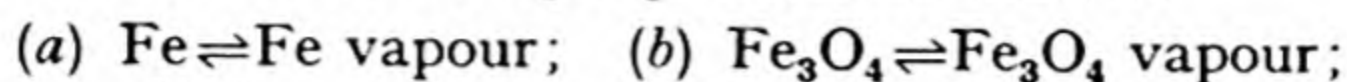
Such cases are termed *heterogeneous* equilibria in distinction from the *homogeneous* type in which all members are present in the same *phase*, that is, are all gases, or substances all in the same solution. The meaning of the term *phase* should be clear from the following tabulation for (1) to (3) above:

Example	(1)	(2)	(3)
Phases:			
solid	2	1	2
gaseous	1	1	1

Since gases are all miscible together no purely chemical equilibrium can contain more than one gaseous phase. In the rare cases in which the solids are freely miscible there would also be only one solid phase, but far more commonly it may be assumed that the number of solid phases is the same as the number of chemically distinct solids present (see further Chapter XIII, 'The Phase Rule').

Since the chemical mechanisms by which equilibria are reached play no part in proving the law of equilibrium, *all* mechanisms, if more than one is possible, must lead to the same point of equilibrium. Now while the vapour pressures of such solids as are included in (1) to (3) above must be very small (except at very high tempera-

tures) they are not *infinitely* small. Example (3) might therefore be dissected into contributory equilibria as follows:



and examples (1) and (2) similarly. The equilibrium (c) is homogeneous, the original heterogeneous character being now confined to (a) and (b).

Expressing for brevity the partial pressures of steam and hydrogen as p_w and p_h and the vapour pressures of iron and its oxide as p_m and p_o , the law of mobile equilibrium applied to equilibrium (c) gives:

$$\frac{p_h^4}{p_w^4} = K_p \cdot \frac{p_m^3}{p_o}.$$

Now the vapour pressure of a solid (or liquid) is fixed by the temperature alone, and does not depend on the amounts present of the volatile or the condensed phase. Therefore:

$$\frac{p_h^4}{p_w^4} = \text{a constant}.$$

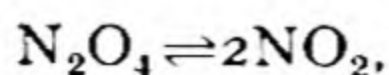
Thus the law leads to the result that in equilibrium (3) the ratio of the pressures of steam and hydrogen is fixed for a given temperature, and to the general conclusion that for members of an equilibrium which are present as pure *solids* no entries need appear in the equilibrium quotient.

For example (1) we have the simple result $p_{\text{CO}_2} = \text{a constant}$. A mixture of chalk and lime, *in any proportions*, behaves like a simple solid in equilibrium with its vapour. For the example (2) the product of pressures $p_{\text{NH}_3} \cdot p_{\text{HCl}}$ is constant at a fixed temperature. It is, of course, extremely improbable that the systems discussed above reach their equilibria principally by the means chosen: direct attack by the gases on the solids at their surfaces is undoubtedly the actual mechanism.

Le Chatelier's Principle. In 1884 the French chemist LE CHATELIER (1850–1936) summarized the qualitative operation of the law of mobile equilibrium in a simple and easily understood rule: *If to a system in equilibrium a constraint is applied, the system tends to adjust itself so as to oppose the constraint and restore equilibrium.* By basing this principle not only upon theory (such as has been briefly illustrated in previous sections), but also on a wide range of confirmatory experiments, Le Chatelier ensured its acceptance and application, continued to the present day.

By 'constraint,' in connection with the present subject, is implied change of pressure, of temperature, or of concentration. In order

to see how the rule is applied to change of pressure we may take the equilibrium:



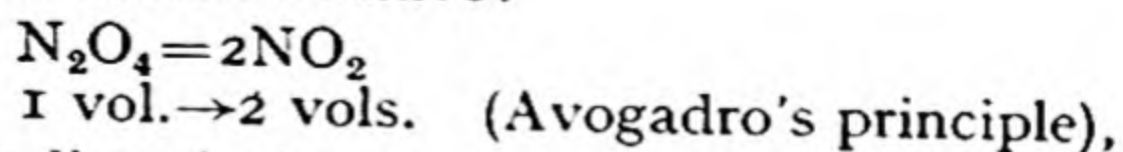
of the type $A \rightleftharpoons 2B$ we have already considered in general terms.



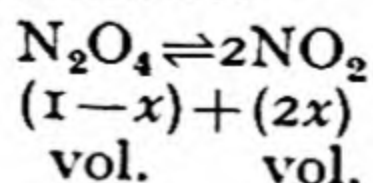
FIG. 31. H. LE CHATELIER

Nitrogen dioxide on cooling liquefies at about 21° , and at -9° the liquid freezes to a nearly colourless solid, which has been shown (by X-ray diffraction) to consist of molecules N_2O_4 . At temperatures above the freezing-point a mixture of NO_2 and N_2O_4 is present in both the liquid and gaseous states. The higher the temperature the more the equilibrium favours the dioxide, until at about 140° the proportion of N_2O_4 is negligible. The *degree of dissociation*, i.e. the fraction of the total number of original N_2O_4 molecules that has dissociated, can be calculated from the observed vapour density of the mixture.

For complete dissociation we have:



and for incomplete dissociation:



if x is the degree of dissociation. Since the vapour density of N_2O_4 is 46, the weight of one litre of the pure gas would be 46 times that of one litre of hydrogen under the same physical conditions of p and T . After the spontaneous dissociation under these conditions the volume of the resulting mixture must be $(1+x)$ litre. The weight of one litre of the mixture relative to hydrogen as before, i.e. its vapour density, is therefore $\frac{46}{1+x}$. The general rule for calculating degree of dissociation x in an equilibrium of the type $A \rightleftharpoons 2B$ is:

$$\frac{\text{Calculated density (of } A\text{)}}{\text{Observed density of mixture}} = 1 + x.$$

For example, if the vapour density of the mixture of N_2O_4 and NO_2 is 30,

$$\frac{46}{30} = 1 + x,$$

whence $x = 0.533$. Alternatively, we may say that N_2O_4 is 53.3 per cent dissociated.

We can predict from the discussion on p. 128 that by applying increased pressure to the gaseous equilibrium $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$, established under pressure p , and thereby decreasing its volume, a shift in the position of the equilibrium ensues, favouring N_2O_4 at the expense of NO_2 . Since two molecules of NO_2 disappear to every one of N_2O_4 formed, this change means that the *total number of molecules in the system decreases*, and by the principles of the kinetic theory such a decrease entails also *decrease* of pressure. To com-

press the initial volume V to, say $\frac{V}{2}$ a pressure of *less than* $2p$ suffices, but if the pressure is actually raised to $2p$ then the volume will contract to less than $\frac{V}{2}$ (see example (5), p. 135).

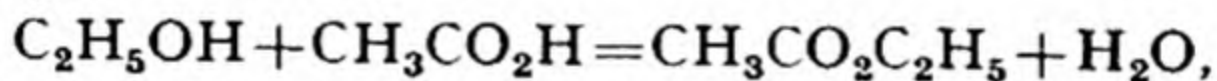
The change in the total number of molecules under increased pressure can only occur when Avogadro's principle, applied to the equation of the reaction, proves a change of volume, as above. In the dissociation of hydrogen iodide $2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2$ (gaseous), an equilibrium readily set up at about 400° , there is no such change of volume; the number of molecules is equal on the two sides of the equation. Hence in this example change of pressure does *not* affect the position of the equilibrium. Le Chatelier's principle in respect to the 'constraint' of change of pressure may therefore be expressed: 'If the pressure on a system in equilibrium is increased then, *if possible*, a chemical change will occur leading to a decrease

in the number of molecules in the system; and conversely for decrease of pressure.'

The Effect of Change of Temperature. (1) The heat of formation of ammonia, $\frac{1}{2}\text{N}_2 + \frac{3}{2}\text{H}_2 = \text{NH}_3$, is -11.0 kcal. and conversely the heat of dissociation of ammonia into its elements is $+11.0$ kcal. Suppose the equilibrium $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ is established at a given temperature, and the temperature is then raised. By Le Chatelier's rule a change will occur if possible which absorbs heat, lowers the temperature, and so 'opposes the constraint.' Obviously this is a partial dissociation of ammonia. Hence the higher the temperature at which equilibrium is set up the lower the proportion of ammonia in the system. This is a very important deduction in relation to the 'fixation' of nitrogen by the synthesis of ammonia (p. 430).

(2) Conversely the heat of formation of nitric oxide, $\frac{1}{2}\text{N}_2 + \frac{1}{2}\text{O}_2 = \text{NO}$, is $+21.6$ kcal. In this case the higher the temperature the better the 'yield' of nitric oxide. Formerly the reaction was used as the basis of one method of nitrogen fixation (the Birkeland-Eyde process), but the costliness of sufficient power to develop the very high temperature required to secure a profitable yield of nitric oxide has led to its abandonment.

(3) The organic reaction between ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$) and acetic acid ($\text{CH}_3\text{CO}_2\text{H}$), yielding the ester ethyl acetate ($\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$) and water,



releases so little heat that it may be considered as *thermoneutral* (cf. p. 116). Hence when equilibrium is reached, Alcohol + acid \rightleftharpoons Ester + water, from a mixture of alcohol and acid in given proportions no better yield of ester is obtained at 100° than at room temperature. In practice, however, the esterification is conducted at the higher temperature, solely because the equilibrium is reached *much more quickly* (p. 177).

In general the *extent* of the shift of equilibrium on change of temperature runs parallel to the *magnitude* of the heat of reaction ΔH .

Change of Concentration. If to a gaseous system in equilibrium more of one of the gases present is added, the equilibrium may or may not be affected. If the gas is added without increasing the volume, then the concentration of that gas in the mixture is obviously increased, and the equilibrium will be shifted accordingly; that is, in such a way as to oppose the constraint applied. Should the gas be added *at its own partial pressure* in the mixture, however, its concentration is unaltered, and the equilibrium is not disturbed.

Quantitative Examples.

(i) Two sealed vessels of quartz glass, the first containing hydrogen and iodine, and the second hydrogen iodide, were heated together at 450° for 12 hours. After quenching in cold water, their contents were analysed. The first contained (in millimol. = $\frac{1}{1000}$ gm.-mol.): hydrogen, 0.52, iodine, 47.48, hydrogen iodide, 39.52; and the second: iodine, 3.17, hydrogen iodide, 25.18.

Calculate the equilibrium constant of the system $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$ at 450° , and explain why you think your calculation gives the true value.

The equilibrium quotient has the form

$$\frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]},$$

and is therefore independent of the volume of the system, and of the unit in which the constituents are expressed.

$$\frac{(39.52)^2}{0.52 \times 47.48} = 63.$$

In the second tube $[\text{H}_2] = [\text{I}_2]$:

$$\frac{(25.18)^2}{(3.17)^2} = 63.$$

Since the equilibrium quotient has equal values true equilibrium must have been reached in each tube, and the constant is 63.

(ii) Calculate the weight in grams of hydrogen iodide produced in the following experiment. A vessel of capacity 1.12 litres, cooled to 0° and containing 2.54 gm. of solid iodine, was filled with hydrogen at atmospheric pressure. After sealing, the vessel was heated at 450° until equilibrium was reached between its contents. For $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$ the equilibrium constant at 450° is 63; the G.M.V. = 22.4 litres at N.T.P.; $I = 127$.

$$\text{Hydrogen} = \frac{1.12}{22.41} = 0.05 \text{ gm.-mol.}$$

$$\text{Iodine} = \frac{2.54}{254} = 0.01 \text{ gm.-mol.}$$

Since the equilibrium quotient is independent of volume, and one molecule of hydrogen and one of iodine give *two* molecules of hydrogen iodide, we have, if x is the hydrogen iodide produced in gm.-mol.:

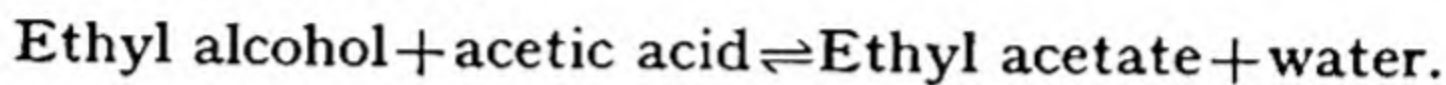
$$x^2 = 63 \times \left(0.05 - \frac{x}{2}\right) \times \left(0.01 - \frac{x}{2}\right),$$

$$\text{or } 59x^2 + 7.56x - 0.126 = 0,$$

from which, by the usual algebraic formula,* $x = 0.015$.

Hence $0.015 \times 128 = \underline{1.92}$ gm. of hydrogen iodide are formed.

(iii) Calculate the percentage yield of ethyl acetate in relation to the amount of acid taken when a mixture of 2 gm.-mol. of ethanol with 1 gm.-mol. of acetic acid is heated at 100° until equilibrium is reached:



The equilibrium constant may be taken as 4.

The equilibrium quotient is independent of volume, and ethyl acetate and water must be produced in equimolecular quantities; therefore if x is the number of gm.-mol. of acetate formed:

$$\frac{x^2}{(2-x)(1-x)} = 4,$$

$$\text{or } 3x^2 - 12x + 8 = 0.$$

$$x = 0.85 \text{ or } 3.15.$$

Since not more than 1 gm.-mol. of acetate can be obtained from 1 gm.-mol. of acid, $x = 0.85$, and the yield is 85 per cent.

(iv) The equilibrium constant of the system $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$ is 63 at 450° . Calculate the free energy ΔG of the reaction $\text{H}_2(g) + \text{I}_2(g) = 2\text{HI}(g)$ at this temperature.

$$\text{We have (p. 127) } \log_e K = \frac{-\Delta G}{RT}.$$

$$\log_e K = 2.30 \log_{10} K = 2.30 \times 1.80 = 4.14.$$

$$R = 1.98 \text{ cal./deg. (p. 33).}$$

$$T = 723^\circ \text{ Abs.}$$

$$\Delta G = -1.98 \times 723 \times 4.14 \text{ calories}$$

$$= \underline{\underline{-5.95 \text{ kcal.}}}$$

(v) At a certain temperature T and a pressure of 1 atmosphere the degree of dissociation of N_2O_4 in the equilibrium $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ is 0.50.

Calculate (a) the degree of dissociation when the mixture of gases is compressed at temperature T to half the original volume, (b) the pressure required to effect this compression.

* A quadratic equation can be solved as follows. If the equation is $ax^2 + bx + c = 0$, then $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$.

(a) If x is the degree of dissociation there are in the equilibrium $1-x$ gm.-mol. of N_2O_4 to $2x$ gm.-mol. of NO_2 , making a total of $1+x$ gm.-mol.

Hence

$$\frac{\left(\frac{2x}{1+x}\right)^2}{\frac{1-x}{1+x}} = K,$$

or

$$\frac{4x^2}{(1-x)} = KV.$$

For $x=0.50$, $KV=2$; after the compression $KV=1$ and for the degree of dissociation x

$$\frac{4x^2}{1-x} = 1.$$

$$4x^2 + x - 1 = 0,$$

whence

$$\underline{x=0.39}$$

(b) For a degree of dissociation x the total number of gm.-mol. of both kinds is $1+x$.

x	$1+x$	Volume
0.5	1.50	V
0.39	1.39	$\frac{V}{2}$

Hence the pressure when $x=0.39$ is $\frac{1.39}{1.50} \times 2 = \underline{1.84 \text{ atmospheres.}}$

CHAPTER XII

SOLUTION

Definitions.

1. A *solution* is a homogeneous mixture of two or more substances. It may be solid, liquid, or gaseous.
2. When two or more substances mix to form a solution, they are said to *dissolve* in one another.
3. In a solution consisting of two substances, the substance present in greater quantity may be called the *solvent*, and that present in smaller quantity may be called the *solute*.
4. If, however, a solid is dissolved in a liquid, it is usual to regard the solid as the solute, even when it forms more than half the weight of the solution. There is, in fact, no real difference between a solute and a solvent; the use of the terms is a mere matter of convenience. Such a distinction is obviously inapplicable to the many pairs of liquids (e.g. ethanol and water) which form homogeneous mixtures in all proportions.
5. The *solubility* of a solid solute in a liquid solvent is usually expressed as the maximum weight in grams of the solute which can be dissolved in 100 gm. of the solvent at the temperature concerned and in presence of excess of solid solute.
6. A *saturated solution* of a solid is a solution the composition of which does not change in presence of the solid solute. An *unsaturated solution* is a solution the concentration of which increases when some of the solid solute is added to it. A *supersaturated solution* is a solution which, on addition of solid solute,* decreases in concentration (by deposition of solute).

Determination of Solubility of a Solid. The solubility of a solid in water at a particular temperature may be determined in the following way. Some distilled water is placed in a beaker or flask together with excess of the solid—preferably in the form of a fine powder. The beaker or flask is supported in a thermostat maintained at the required temperature, and the liquid is thoroughly stirred until a saturated solution is presumably formed; about 2 or 3 hours will generally be sufficient.

By means of a pipette—previously warmed or cooled to the

* Or of some substance isomorphous with it.

temperature of the thermostat, and carrying a glass extension fitted with a plug of glass wool to prevent the accidental taking-up of solid solute particles—a suitable volume of the saturated solution is transferred to a weighed weighing-bottle. The weight of the bottle and solution is found, after which the solution is carefully evaporated to dryness and the residue weighed.

Alternatively, if the solute can be estimated volumetrically, the weighed solution is transferred to a graduated flask and made up to a known volume with distilled water. The concentration of the diluted solution is then determined by a titration. The solubility

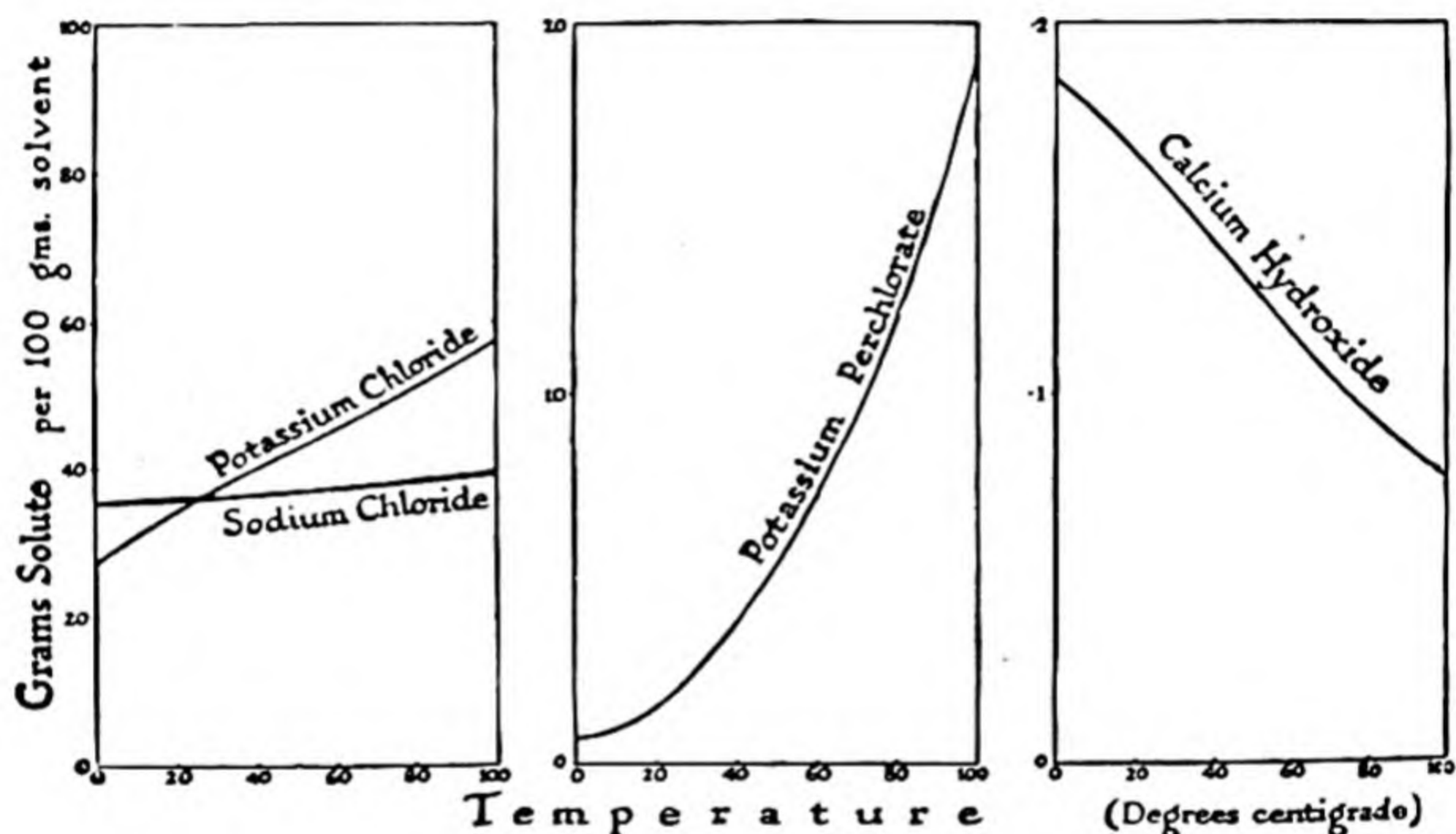


FIG. 32. TYPES OF SOLUBILITY CURVES

of common salt, for example, may be found in this way, using standard silver nitrate solution. The solubility of hydrated substances, e.g. $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, is expressed as grams of *anhydrous* substance (e.g. Na_2SO_4) per 100 grams of water.

Most so-called 'insoluble' substances are really slightly soluble. If they are electrolytes (e.g. salts) their solubility may be estimated by measurements of the conductivity of the solution.

Solubility Curves. If the solubilities of a substance in a given solvent at various temperatures are plotted against those temperatures, the curve so obtained is a *solubility curve*. Typical examples of solubility curves are shown in Fig. 32. The solvent here is water.

Reference to the figure will show that with some substances the solubility increases with rise of temperature, and this is indeed the most frequent occurrence. It follows from LE CHATELIER'S

principle (p. 130) that such substances should dissolve in water with absorption of heat: a deduction borne out in practice.

Other substances, such as calcium hydroxide, citrate and normal butyrate, and cerous sulphate, decrease in solubility with rise of temperature, while the solubility of common salt varies but little between 0° and 100° .

Sodium sulphate shows a solubility curve with a sharp break at 32.4° . Actually it is not a single curve, but consists of two curves which intersect at the break. The left-hand part is the solubility curve of sodium sulphate decahydrate, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$; at 32.4° , however, the decahydrate splits up into water and anhydrous sodium sulphate, Na_2SO_4 , and the right-hand part is the

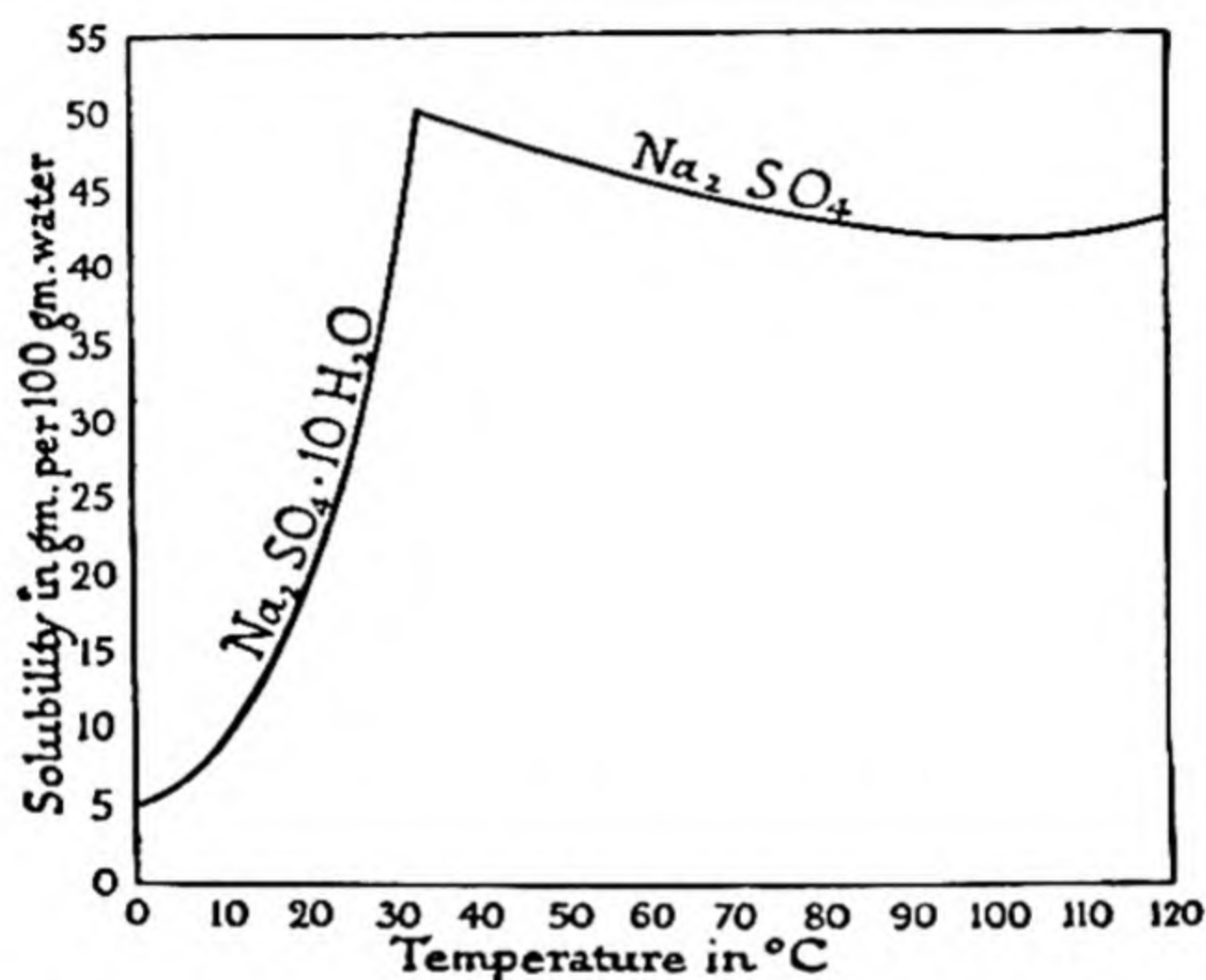


FIG. 33. SOLUBILITY CURVE OF SODIUM SULPHATE

solubility curve of the anhydrous salt. At temperatures above 32.4° , a saturated solution of sodium sulphate will on evaporation deposit crystals of Na_2SO_4 ; below 32.4° , crystals of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ are deposited.

It should not be overlooked that all solubilities in Fig. 33 are in terms of *anhydrous* sodium sulphate, Na_2SO_4 . A solution saturated with the decahydrate (G.F.W.=322) at 20° contains 19.4 gm. of Na_2SO_4 (G.F.W.=142) per 119.4 gm. of *solution*, and could be prepared by dissolving $19.4 \times \frac{322}{142} = 43.7$ gm. of the hydrate in $119.4 - 43.7 = 75.7$ gm. of water at 20° . A solution identical in all

its properties (chemical composition, density, refractive index, etc.) would be obtained by dissolving 19.4 gm. of the anhydrous salt in 100 gm. of water at 20°. The break in the solubility curve is thus associated solely with change of the *solid* in contact with the solution, and not with any difference in the nature of the solution. Conversely, the existence of breaks in a plot of solubilities is one of the surest indications of change, for example from one hydrate to another, in the solid phase.

The steep *upward* slope of the curve for the hydrate implies that the dissolution is strongly *endothermic*, and the lesser *downward* slope of the other curve that the dissolution of anhydrous salt is slightly *exothermic* (Le Chatelier's principle). These deductions suggest that the dissolution of anhydrous salt includes its hydration, and that this is a strongly exothermic process, for in the decahydrate such hydration is evidently already largely accomplished even in the solid crystal.

The Transition Point. At the unique temperature (32.4°) defined by the intersection of the branches of the solubility curve the solution is simultaneously saturated by, i.e. in equilibrium with, the decahydrate and the anhydrous salt. When to the system at this temperature, consisting of the solution and excess of each of the solids, heat is admitted *no change of temperature can occur* until all hydrate is converted into anhydrous salt. Only after this endothermic change is complete will the temperature rise and a limited further amount of anhydrous salt be deposited, as the composition of the solution follows the downward sloping curve. Conversely, when heat is withdrawn, no change of temperature occurs until all anhydrous salt has been hydrated. It should now be clear why the point of intersection of the parts of the solubility curve is termed the *transition point* of the system.

On allowing a saturated solution prepared at about 40° to cool slowly in contact with solid, the transition system at 32.4° is usually set up spontaneously; if not, a 'seeding' with a crystal of decahydrate is effective. A very long temperature 'arrest' then ensues, often lasting in heat-insulated vessels up to one hour, before the fall of temperature is resumed, and the composition of the solution follows the steep downward curve, with deposition of decahydrate. Many hydrated salts behave similarly at their specific transition points, and because of the ease with which the transition systems can be set up and the complete fixity of their temperatures they are widely used as a means of standardizing thermometers: some examples are:

$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} / \text{Na}_2\text{SO}_4$	32.383°
$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O} / \text{Na}_2\text{S}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$	48.45°
$\text{NaBr} \cdot 2\text{H}_2\text{O} / \text{NaBr}$	50.674°

The Eutectic Point. If a dilute aqueous solution is partially frozen, the solid which separates is generally pure ice; the remaining liquid is therefore a more concentrated solution. On further freezing, a point is at length reached when the unfrozen portion is a saturated solution, and this then freezes as a whole. The temperature at which freezing takes place falls continuously during this process, but when the residual liquid freezes as a whole, the temperature remains constant at a minimum value. This point is called the *eutectic point*, and the solution solidifying as a whole is called the *eutectic mixture*.

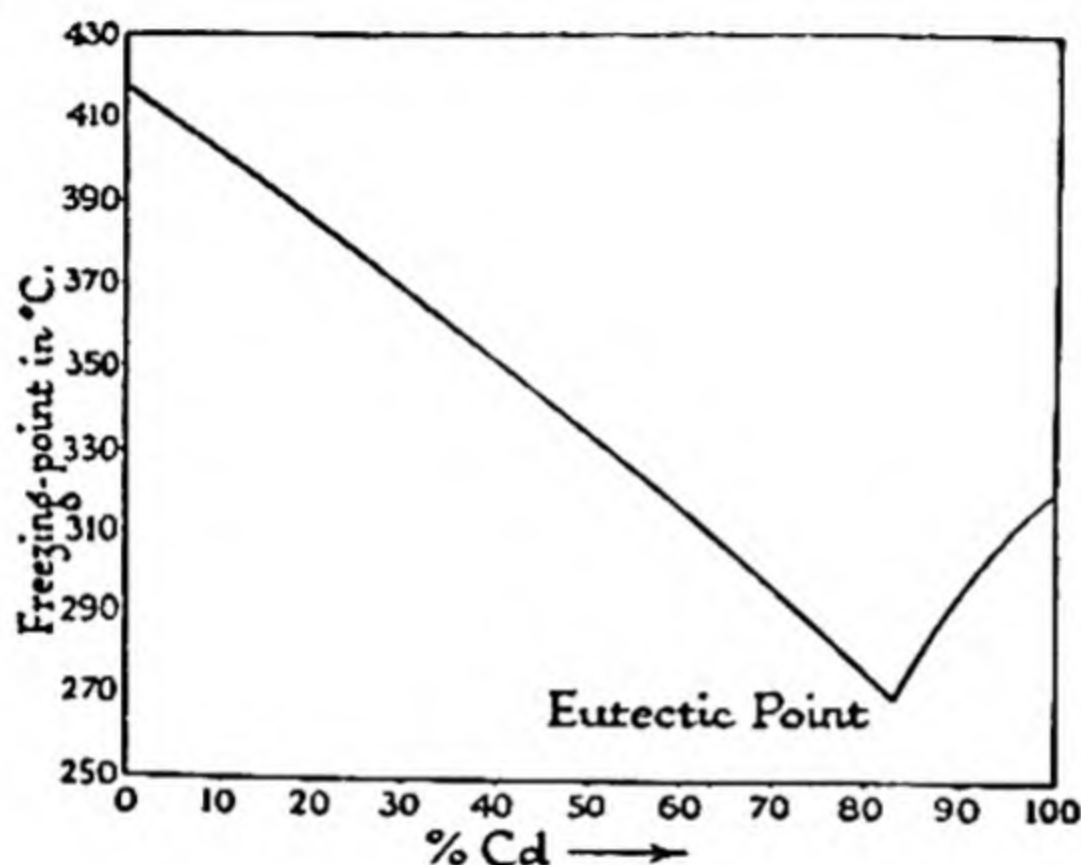


FIG. 34. FREEZING-POINT DIAGRAM FOR Zn-Cd ALLOYS

GUTHRIE, who in 1875 first observed that an aqueous solution of a salt froze as a whole at a definite temperature, mistook the solid formed for a *hydrate* of the dissolved salt, since it simulated a pure substance not only in melting at the same fixed and specific temperature but also in forming at that temperature a liquid of the same composition as itself. He proposed the terms *cryohydrate* and *cryohydric temperature*.^{*} Later it was proved that the solid consisted of an intimate mixture of ice and salt crystals, but the epithet *cryohydric* has survived as convenient in referring to eutectic phenomena in aqueous solutions. The example is instructive in showing that a solid which melts at a fixed temperature to a liquid of its own composition is not proved by these facts alone to be a pure substance.

Similar eutectic points are shown by many solutions, e.g. an alloy of zinc and cadmium has a eutectic point at 270°, the composition of the eutectic mixture being roughly 83 per cent Cd, 17 per cent Zn. A molten alloy of zinc and cadmium containing more than 83

^{*} From Greek *kryos*, icy cold.

per cent Cd will on cooling yield crystals of cadmium until the composition of the still liquid portion corresponds to the eutectic mixture; this will then solidify as a whole, at 270° . (See further, Chapter XIII.)

Purification by Re-crystallization. Re-crystallization from a suitable solvent is the method most relied upon for the purification of crystalline solids. As an example we describe the removal, on the laboratory scale, of 5 per cent of potassium chloride from potassium perchlorate, KClO_4 . The relevant solubilities are:

	Potassium perchlorate	Potassium chloride
100°	18.7	56.5
20°	1.6	34.0

Into 50 c.c. of boiling water, contained in a conical flask, 10 gm. of the 'crude' perchlorate are introduced: most of the solid soon dissolves, since at 100° 50 gm. of boiling water dissolves 9.4 gm. of the pure perchlorate. Further small amounts of hot water are cautiously added until, after shaking well the flask with its contents, all solid is just dissolved. The 'yield' of the pure salt depends entirely on the care taken to secure a *saturated* solution in the *boiling* solvent.

The flask is now corked to prevent evaporation and set aside to cool spontaneously to room temperature (say 20°). A crop of crystals of the perchlorate steadily accumulates, which will be free from chloride: the solubility of the latter in 50 gm. of water at 20° is 17.0 gm. and although the presence of the other salt will somewhat diminish this, it certainly will not reduce it to 0.5 gm. in 50 gm. of water. The contents of the flask are now cast on to a suction filter, and the 'mother liquor' drained away as completely as possible. The crystals on the filter are then moistened with say 5 c.c. of *cold* water and the liquid sucked through the filter. Mother liquor adhering to the crystals and containing chloride is thus removed. After drying, the crop of pure perchlorate should weigh about 9.0 gm., a loss of one gram being the price of purification. A solution of a sample in water gives no trace of precipitate with aqueous silver nitrate (silver perchlorate is very soluble in water).

Water as a Solvent. When a crystalline solid dissolves in a liquid the molecules (or ions) bound to each other in the crystal in an arrangement of almost perfect order become distributed at random in the solution. The breaking up of the crystal requires an input of energy, and the dissolution is therefore nearly always endothermic, but simultaneously full scope is given to the tendency of order (in the crystal) to pass into disorder (in the solution), i.e. there

is a relatively large increase of *entropy* and this is the principal reason why a solid dissolves in a liquid.

The constitution of water has already been described (p. 118), and it is this constitution and the polar property of its molecules giving rise to it that determine the power of water as a solvent. Only substances that can break down, or at least strongly affect, its closed, hydrogen-bonded formation can dissolve freely in water. Amongst gases only those which have themselves highly polar molecules—e.g. ammonia, hydrogen chloride, sulphur dioxide—dissolve freely; those solid covalent compounds that dissolve easily in water—e.g. sugars, urea, many organic acids—contain either hydroxy groups —OH or other similar groups such as —NH₂ that can also form hydrogen bonds and so become incorporated in the water system. The relatively low melting-points and boiling-points of the majority of covalent compounds show that in their solid and liquid forms the intermolecular attractions are small, but in spite of this they dissolve to only a limited extent in water because they are unable to disturb its closed formation.

It is upon *ionic compounds* that water exerts its most striking action as a solvent (p. 111). In the table, under the symbol *L*, are given the *lattice energies* (p. 104) of some metallic chlorides. These are the energies required to dissociate a gram-formula weight into

Salt	NaCl	KCl	NH ₄ Cl	RbCl	CsCl
<i>S</i> _{15°}	0.61	0.48	0.66	0.70	1.08
<i>L</i>	183	165	157	161	152
ΔH_s	1.3	4.4	4.0	4.2	4.6

* *S*_{15°} = Solubility at 15° in G.F.W. per 100 gm.

L = Lattice energy of crystal (kcal.).

ΔH_s = Heat of solution per G.F.W. (kcal.).

its ions (e.g. Na⁺ and Cl⁻) and separate them widely from each other. Such a process occurs in dissolution, and if no further action intervened the (endothermic) heat of solution ΔH_s would differ little from these lattice energies, which are overwhelmingly greater than the possible increase in the entropy term $T\Delta S_s$ in the relation:

$$\Delta G_s = \Delta H_s - T\Delta S_s \text{ (p. 124).}$$

No possibility of a decrease of free energy *G_s* could emerge, and therefore no spontaneous dissolution in the solvent could occur. There must therefore be a source of energy *release* during dissolution potent enough to compensate the large lattice energy: this lies in the *hydration* of the ions. The polar water molecules become strongly bound to both cations and anions: to the former by the negatively charged oxygen, and to the latter by the oppositely charged hydrogen, and in this action of *hydration* a very large amount of

energy is released. The heat of solution is thus a small difference between two very much larger heat quantities. From the table it can be seen how nearly the heat of hydration compensates the lattice energy, by comparing L with ΔH_s , the heat of solution per G.F.W. The fact that the maximum densities of even dilute salt solutions lie at the freezing-point indicates how largely the hydrogen bonding in pure water is disturbed (p. 118). As is well known many crystalline salts retain their hydration in the solid state as 'water of crystallization.' It will be noted that the unusually low heat of solution of sodium chloride accounts for the small increase of its solubility with rise of temperature (p. 138). A few other liquids with polar molecules can freely dissolve ionic compounds for similar reasons; such are hydrogen peroxide (B.P. 155°), hydrogen fluoride (B.P. 19°), sulphur dioxide (B.P. -10°) and ammonia (B.P. -33°). Such liquids are often called *ionizing solvents*, but the term is open to some objection, as it might imply that ionization is brought about by the dissolution, when in fact this merely frees from each other the ions already present in the crystal.

The Influence of Ionic Size. The investigation of crystals of ionic compounds by X-ray diffraction has enabled ionic radii to be determined.

Ionic radii (cm. $\times 10^{-8}$)							
Cations				Anions			
Li ⁺	0.78			O ²⁻	1.32	F ⁻	1.33
Na ⁺	0.98	Mg ²⁺	0.78	S ²⁻	1.74	Cl ⁻	1.81
K ⁺	1.33	Ca ²⁺	1.06			Br ⁻	1.95
NH ₄ ⁺	1.43					I ⁻	2.16
Rb ⁺	1.49	Sr ²⁺	1.27				
Cs ⁺	1.65	Ba ²⁺	1.43			H ⁻	1.27

A comparison of the above table with that of solubilities (p. 143) shows that lattice energy and hydration energy both decrease with increasing radii of the cation; and the further sample of data:

	KCl	KBr	KI
L	165	155	144 (kcal. per G.F.W.)
ΔH_s	4.4	5.1	5.1 (kcal. per G.F.W.),

confirms that increase of anionic size has a similar effect.

Such a relation is to be expected, for if the inverse square law for electrical forces is assumed to hold for unlike ions of radii r_+ and r_- in contiguity, then the energy required to separate them is (product of charges) \div (distance between ionic centres) $= \frac{e^2}{r_+ + r_-}$. The power of an ion to attract and bind water molecules depends on the

density of electric charge on its surface $= \frac{e}{4\pi r^2}$ (for spherical ions).

The smaller the ion the greater its hydration. This accounts for the surprising fact that in electrolysis (Chapter XVI) the rubidium ion Rb^+ travels faster than a lithium ion Li^+ although in the anhydrous state the latter has only half the radius of the rubidium ion.

The size of a cation often determines the chemical behaviour of salts in which it occurs. Unlike the corresponding salts of all other metals the carbonates of the alkali metals are stable to heat, and their nitrates lose only oxygen, to give nitrite. To these characteristics lithium is an exception, for its carbonate and nitrate on heating both readily yield the oxide Li_2O . In spite of its minimal ionic charge the lithium ion is so small and electrically powerful that it extracts an oxygen ion O^{2-} from the much larger carbonate CO_3^{2-} and nitrate NO_3^- , causing their decomposition.

The Solubility of Gases in Liquids. At constant temperature, *the weight of gas dissolved by a given volume of a liquid is proportional to the pressure of the gas*—a fact which was discovered experimentally by HENRY in 1803 and is known as *Henry's Law*.* At pressure p a given quantity of liquid dissolves w grams of gas, occupying a volume V at that pressure. At pressure $2p$ the same quantity of solvent dissolves $2w$ grams of gas: but from Boyle's Law this weight of gas occupies at the increased pressure the same volume V as before. It follows that, at constant temperature, the *volume* of a gas dissolved by a fixed volume of liquid is constant. The *solubility of a gas* may be defined as *the number of c.c. of the gas required to saturate 1 c.c. of the solvent at the temperature concerned*. Alternatively, the solubility of a gas can be expressed in terms of its *absorption coefficient*, which is the volume in c.c. of the gas, *reduced to N.T.P.*, required to saturate 1 c.c. of solvent. The advantage of the absorption coefficient is that it is proportional to the number of *gram-molecules* of gas dissolved per unit volume of solvent.

Applying Dalton's Law (p. 25) with Henry's Law to the solubility of a mixture of gases in a solvent, we see that *the volume of each individual gas dissolved, after reduction to N.T.P., will be proportional to the partial pressure of that gas in the mixture*.

Example: The absorption coefficients of nitrogen and oxygen in water at 0° are 0.024 and 0.049 respectively. If dry air, taken as 79 per cent nitrogen and 21 per cent oxygen by volume, is shaken up with 1,000 c.c. water at 0° and 1 atmosphere pressure, what volume of each gas will dissolve?

* Henry's Law does not apply to very soluble gases.

When the gas is at atmospheric pressure, 1,000 c.c. of water dissolve $0.024 \times 1,000$ c.c. of nitrogen; but the pressure of the nitrogen is only 0.79 atmosphere. Hence the volume of nitrogen dissolved, corrected to N.T.P., is $24 \times 0.79 = 19.0$ c.c.

Similarly, the pressure of the oxygen is 0.21 atmosphere; hence the volume of oxygen dissolved, corrected to N.T.P., is $0.049 \times 1,000 \times 0.21 = 10.3$ c.c.

(If the dissolved gas were boiled out, it would therefore consist of nitrogen and oxygen in the proportion of 19 to 10.3 by volume, i.e. 65 per cent nitrogen, 35 per cent oxygen.)

The solubility of all gases diminishes with rise of temperature, and many gases may be completely expelled from their aqueous solution by boiling. In other cases, however, a point may be reached on heating at which the gas and water are simultaneously

vaporized from the solution in the exact proportion in which they are present in it. This means that the solution will then boil as a whole; such a 'constant-boiling mixture' is formed, for example, when hydrochloric acid is boiled (p. 549)—it contains 20.2 per cent HCl and boils at 110° under a pressure of 760 mm. The composition of a constant-boiling mixture varies slightly, however, with the external pressure. Constant-boiling mixtures are also termed 'azeotropic* mixtures.'

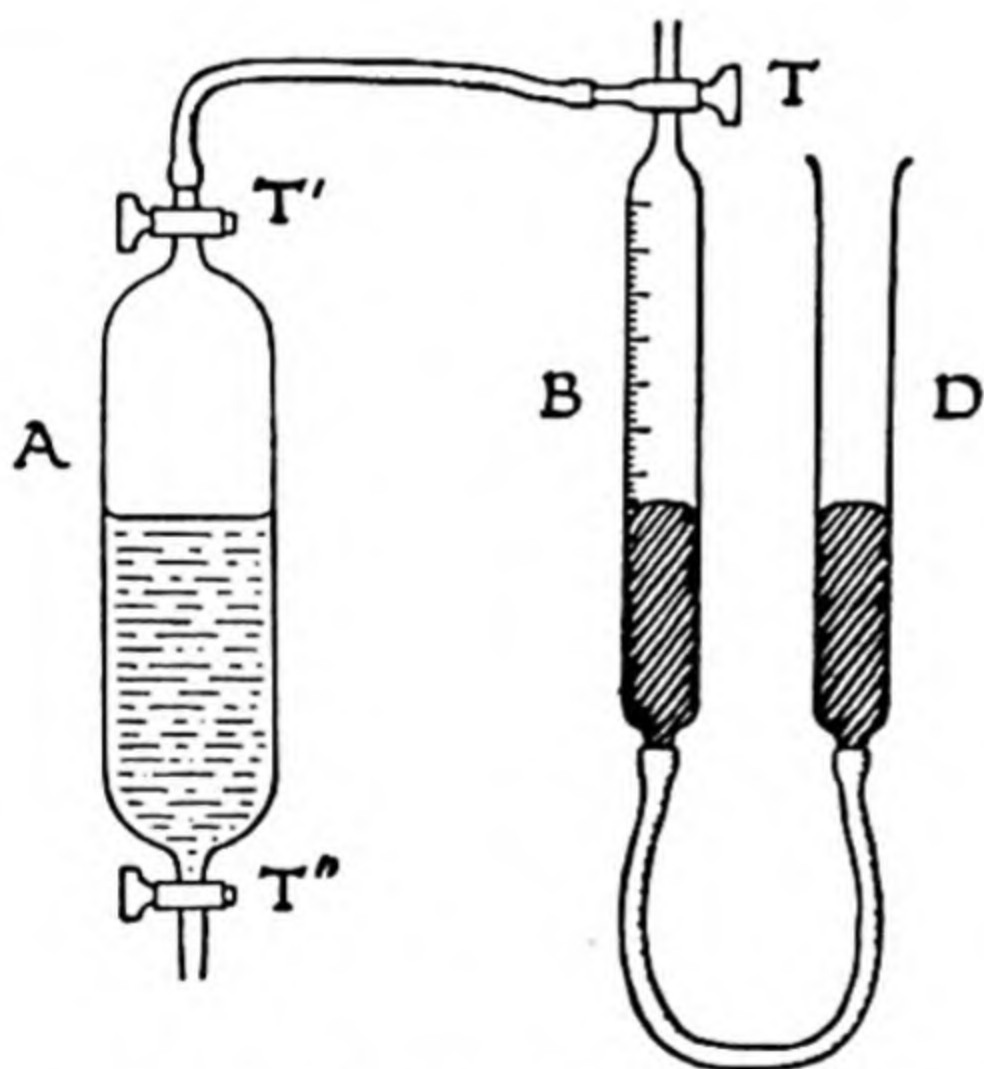
Measurement of Solubility of Gases in Water.

(i) *Slightly soluble gas.* The apparatus employed is shown in Fig 35.

FIG. 35. PIPETTE FOR MEASURING SOLUBILITY OF A SLIGHTLY SOLUBLE GAS

The tube B, and the connecting tube TT', are filled with the gas, the pressure of which is made atmospheric by raising or lowering D until the level of the mercury is the same in both limbs. The bulb A, of known capacity, V c.c., is filled with air-free distilled water.

* Greek, *zeō*, to boil: 'azeotropic' may be translated as 'not boiling in the usual way.'



A known volume, x c.c., of the water is run out of A through T'', and at the same time D is raised so that gas passes from B through T' into A. T' is then closed and the bulb A vigorously shaken. T' is again opened, and the levels in B and D are equalized. The diminution in volume shown in B is the volume of the gas dissolved in $V-x$ c.c. of water. The apparatus should be maintained at a constant temperature, e.g. in a thermostat.

(ii) All very soluble gases are chemically reactive, hence their solubility is measured by preparing a saturated solution, diluting a measured weight of it to a suitable known volume, and then titrating with an appropriate standard solution.

Distribution of a Gas between Solvents. Henry's Law is expressed as $w=k.p$, where p is the pressure of the gas, w is the weight of gas dissolved in a volume V of solvent, and k is a constant. The concentration of the gas (gm./c.c.) in the solution is $\frac{w}{V}$. If the pressure is doubled, $2w$ gm. dissolves in the volume V , and the concentration is $\frac{2w}{V}$. It is clear that Henry's Law leads to the relation (concentration of dissolved gas) = (constant) \times pressure, or $C=k'p$, the constant k' varying with the solvent.

Arbitrary volumes of two immiscible solvents A and B (e.g. water and benzene) are *separately* shaken with a gas G at the same pressure p until each liquid is saturated. Then $C_A=k'_A.p$, and $C_B=k'_B.p$, that is

$$\frac{C_A}{C_B} = \text{constant.}$$

On now bringing the two solutions into contact in the absence of the gas they will clearly be in equilibrium, and no change of concentrations will occur. We might have achieved the same result more expeditiously by shaking the two liquids simultaneously with the gas. Since, in arriving at the result $\frac{C_A}{C_B} = (\text{constant})$, the pressure cancels out, that expression must correspond to a general rule of distribution of the gas between the solvents at all pressures, and for all volumes of the solvents. We shall see below that this rule of distribution, so simply proved for gas solutions, is valid quite generally for the distribution of solutes that are liquid or solid.

The General Distribution Law. If two non-miscible liquids, A and B (e.g. chloroform and water), are placed in contact with one another, and a substance, C, soluble in each of them is now added, it is found that some of the solute dissolves in each of the liquids. Moreover (supposing that the solutions are not saturated) the distri-

bution of the solute between the two liquids is such that the ratio $\frac{\text{concentration of C in A}}{\text{concentration of C in B}}$ is constant—at constant temperature—for the particular solvents and solute employed.

This fact is known as the *partition law*, and the constant ratio is the *partition coefficient* or *distribution coefficient*. The value of this coefficient for the solute iodine and the immiscible liquids toluene and water is: $\frac{\text{concentration in toluene}}{\text{concentration in water}} = 52$. Suppose we

take a litre of toluene and a litre of water, and dissolve 20 gm. of iodine in the 'mixture.' Then, if x is the concentration of the iodine-toluene solution, and $20-x$ the concentration of the iodine-water solution, in grams of iodine per litre, we have:

$$\frac{x}{20-x} = 52$$

$$\therefore x = 19.6.$$

That is, 19.6 gm. of the iodine will dissolve in the litre of toluene and 0.4 gm. in the litre of water.

When values for the distribution ratio of acetic acid between benzene and water are determined, it is found that they are by no means constant. The ratio $\frac{(\text{concentration in water})^2}{\text{concentration in benzene}}$, is, however, more nearly constant. The explanation of this apparent anomaly will shortly appear.

We saw on p. 126 that the molar free energy of an ideal gas could be expressed either in terms of the pressure p :

$$(1) \quad G_T = RT \log_e p + G_0,$$

G_0 being the molar free energy at *unit pressure*; or in terms of molar concentration C :

$$(2) \quad G_T = RT \log_e C + G_0,$$

G_0 then being the molar free energy at *unit concentration*. Here again we assume that the molar free energy of a *solute in dilute solution* can be expressed in the form (2). The molar free energy at unit concentration will, of course, differ from one solvent to another.

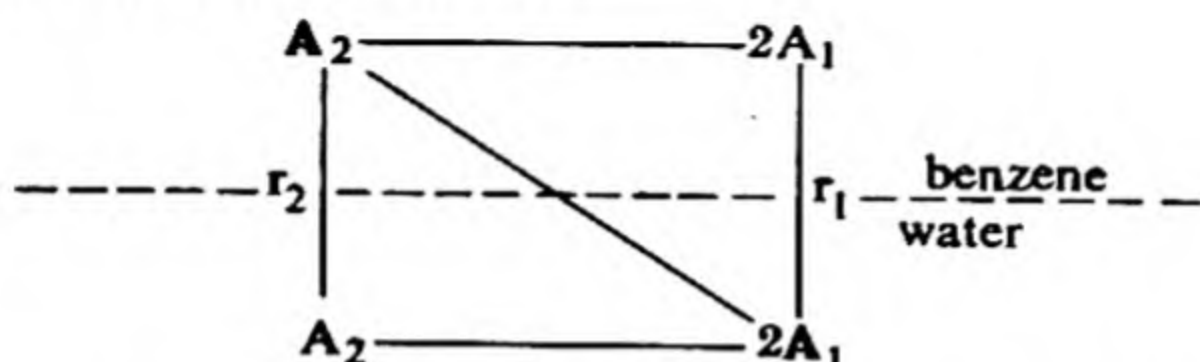
If we dissolve a solute S in one solvent A and then shake the solution with a second immiscible solvent B , the system soon reaches a distribution equilibrium, because, as for all equilibria, the free energy of the system has decreased to its minimum. Following the line of reasoning on p. 127 we consider the situation when a small fraction x of a gram.-molecule of S has still to pass from solution in A to solution in B to attain the equilibrium condition. For this small final transit of S we must have:

$$-x[RT \log_e C_A + (G_0)_A] + x[RT \log_e C_B + (G_0)_B] = 0;$$

whence $\log \frac{C_B}{C_A} = \frac{(G_0)_A - (G_0)_B}{RT} = \text{constant}$, at constant temperature,

and the distribution ratio $\frac{C_B}{C_A}$ is therefore also constant at fixed temperature.

Acetic Acid in Water-benzene.



By the cryoscopic method shortly to be described (p. 159) it can be proved that the molecular weight of acetic acid dissolved in water is close to 60, corresponding to the formula $C_2H_4O_2$; and that in benzene solution the molecular weight is close to double this value. Hence we must suppose that in the latter solution the acid strongly tends to form *dimeric* molecules $(C_2H_4O_2)_2$, and that such a tendency is barely detectable in water solution. The vapour density of acetic acid near its boiling-point is notably greater than 30. The situation in the partition of acetic acid between water and benzene is shown diagrammatically in the diagram, wherein the single line — is used for the equilibrium sign \rightleftharpoons , and predominant molecular species are identified by heavy type.

Since two substances mutually in equilibrium with a third must themselves be in equilibrium we see that the *monomeric* acid A_1 in water and the *dimeric* acid A_2 in benzene stand in chemical equilibrium, to which the general law can be directly applied:

$$\frac{[A_1]^2 (\text{water})}{[A_2] (\text{benzene})} = K_c.$$

This result follows *only* because the monomeric and dimeric forms of the acid both obey the general distribution law:

$$\frac{A_1 (\text{benzene})}{A_1 (\text{water})} = r_1 \text{ (a small ratio), and } \frac{A_2 (\text{benzene})}{A_2 (\text{water})} = r_2 \text{ (a larger ratio).}$$

The experimental ratio $\frac{(\text{concentration in water})^2}{(\text{concentration in benzene})}$ is not strictly constant since it ignores the small but definite amounts of monomeric molecules in benzene and of dimeric molecules in water.

OSMOSIS AND OSMOTIC PRESSURE

Osmosis. If a bladder is filled with a concentrated aqueous solution of sugar and immersed in water, it gradually swells, owing to the passage of water from without to within, and finally bursts. The phenomenon can be studied in a less messy and catastrophic manner by tying a piece of parchment or cellophane over the mouth of a long thistle-funnel, inverting the funnel, partially filling it with the sugar solution, and immersing its head in a vessel of water. The level of the liquid in the funnel gradually rises and may reach a considerable height.

The passage of the water through the membrane into the solution is called *osmosis*.* The membrane is described as *semi-permeable*, since the water molecules can pass through it very much more quickly than the sugar molecules; the latter do, however, slowly penetrate it (p. 257), and the liquid in the stem of the funnel steadily falls, after reaching a maximum height, until the levels are the same inside and outside. At this point the concentration of the liquid in the vessel is the same as that of the liquid in the funnel. If a 'perfect' semi-permeable membrane could be found, which entirely prevented the passage of sugar molecules through it, the column of liquid in the stem of the funnel would remain constant at its maximum height. This height would correspond to the true *osmotic pressure* of the solution finally remaining in the funnel.

The phenomenon of osmosis is not confined to a sugar solution and water, but is shown (a) when any solution is separated from its pure solvent by a semi-permeable membrane, (b) when two solutions, containing the same solvent, with different molecular concentrations of solute—that is, with different numbers of gram-molecules of solution per litre—are separated by a semi-permeable membrane.

Solutions with the same osmotic pressure are said to be *isotonic*.

Semi-permeability. The simplest, and for solutions of solids the most perfect, partition between solvent and solution is the *vapour of the solvent*. Into a glass capillary tube two short 'threads,' one of a solution and the other of its solvent, are introduced so that they are separated by a short interval of vapour (mixed with air). When the tube, kept at a constant temperature, is inspected from time to time under the microscope the thread of solution is seen to be lengthening continuously at the expense of the solvent thread, and ultimately all the latter disappears. In such an experiment *osmosis* occurs but there is no direct evidence of the existence of an *osmotic pressure*.

* Greek, *ōsmos*, a push.

Continuous liquid or semi-liquid partitions, such as the gelatinous copper ferrocyanide membrane favoured by many investigators, undoubtedly operate by *differential solubility* of the *solvent* in the membrane; it is less soluble on the solution side, and a slow but continuous flow of solvent into solution must occur across the partition. Solid membranes, such as 'cellophane,' which have recently come into use (p. 161) act as *molecular 'sieves,'* for they are permeated by a multitude of holes too small to allow the passage of large molecules. It is important to realize that *any* perfect partition, whatever its mode of action, will allow the observation of the true osmotic pressure, but its nature may very greatly influence the time required for the maximum pressure to develop.

Measurement of Osmotic Pressure. Osmotic pressures may be very high, and are thus difficult to measure directly, since the membrane is likely to burst. A method employed by PFEFFER, and later by MORSE and FRAZER, was to deposit a membrane of copper ferrocyanide in the pores of a porous pot. This was then filled with the solution to be examined, and attached to a manometer. On surrounding the pot with a beaker of the pure solvent, the osmotic pressure developed could be read off. The mechanical

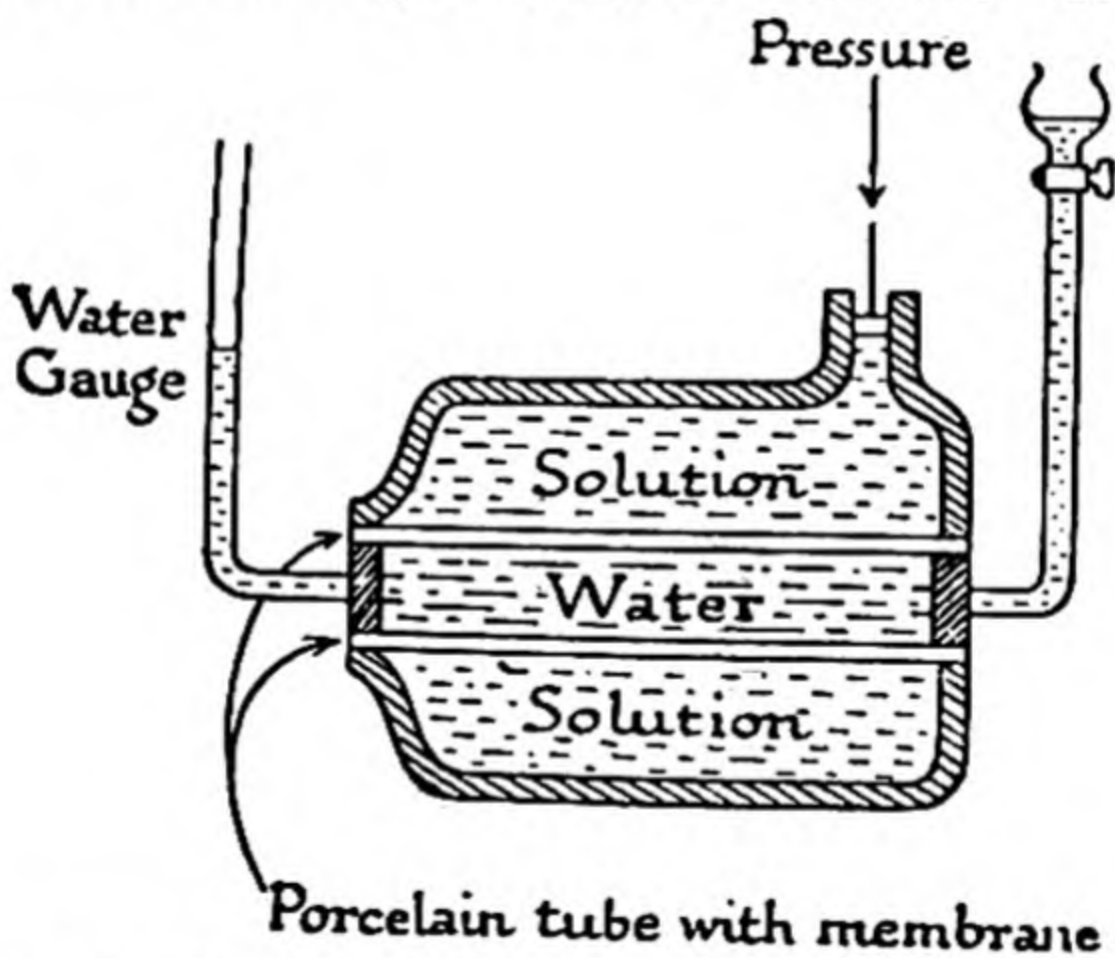


FIG. 36. BERKELEY AND HARTLEY'S APPARATUS

support afforded to the membrane by the porous earthenware enables high pressures to be reached before rupture occurs.

A different method was employed by BERKELEY and HARTLEY, who used the apparatus shown diagrammatically in Fig. 36. The copper ferrocyanide membrane was supported, as before, in the pores of an unglazed porcelain tube, but Berkeley and Hartley

applied pressure, as indicated in the figure, to prevent water from passing into the solution. The pressure was continuously raised until the level of the water in the gauge showed no further tendency to drop, and the maximum pressure required was regarded as equal to the osmotic pressure of the solution. The outer case of the apparatus was made of stout metal.

Magnitude of Osmotic Pressure. Pfeffer observed that, at constant temperature, the osmotic pressures of dilute solutions of the same solvent and same solute were proportional to the concentration. For solutions of sucrose (cane-sugar) in water he obtained the following figures:

<i>Concentration of Sucrose in gm. per 1000 c.c.</i>	<i>Osmotic Pressure in mm.</i>	$\frac{O.P.}{Conc^n.}$
1	53.5	53.5
2	101.6	50.8
4	208.2	52.0
6	307.5	51.3

Closer constancy for the ratio osmotic pressure/concentration is shown by Berkeley and Hartley's figures for similar solutions:

<i>Concentration of Sucrose in gm. per litre</i>	<i>Osmotic Pressure in atmospheres</i>	$\frac{O.P.}{C.}$
10.00	0.65	0.065
20.00	1.27	0.064
45.00	2.91	0.065
93.75	6.23	0.067

Pfeffer also discovered that the osmotic pressure of a given solution is directly proportional to its *absolute temperature*, a discovery confirmed by Morse and Frazer and other workers. Some of Morse and Frazer's figures, for a particular sucrose solution, are given below:

<i>Osmotic Pressure, P, in Atmospheres</i>	<i>Absolute Temperature, T.</i>	$\frac{P}{T}$
7.085	273	0.026
7.334	283	0.026
7.605	293	0.026
7.729	298	0.026

VAN'T HOFF in 1887 pointed out that Pfeffer's results indicated a *formal* similarity between osmotic pressure and gas pressure, for the constancy of the ratio osmotic pressure/concentration is exactly analogous to the constancy of the product PV in the case of a gas

(Boyle's Law). V , the volume of a given mass of gas, is inversely proportional to its concentration, so that Boyle's Law might equally correctly be written $\frac{P}{C} = \text{a constant}$.

In the same way, the constancy of the ratio osmotic pressure/absolute temperature is analogous to that of the ratio P/T for gases.

These facts are sufficiently important to be re-stated as follows:

(i) *At constant temperature, the osmotic pressure of dilute solutions of the same solute in the same solvent is directly proportional to the concentration and therefore inversely proportional to the volume:*

$$P/C = PV = \text{a constant.}$$

(ii) *At constant concentration (i.e. at constant volume) the osmotic pressure of a solution is directly proportional to its absolute temperature.*

$$P/T = \text{a constant.}$$

van't Hoff further observed that *the osmotic pressure of a solution is the same as the pressure which the solute would exert if it existed as a gas at the same temperature and occupied the same volume as the solution, i.e. the G.M.W. of a solute in 22.4 litres of solution gives an osmotic pressure of 760 mm. at 0° C.*



FIG. 37. J. H. VAN'T HOFF

E.N.A.

For example, the M.W. of sucrose, $C_{12}H_{22}O_{11}$, is 342. Hence if sucrose could be obtained as a gas at N.T.P., 342 gm. of it would occupy 22.4 litres. Now Berkeley and Hartley found that 10 gm. of sucrose in a litre of solution gave an osmotic pressure of 0.66 atmospheres at 0°. Then 22.4 litres of such a solution, possessing the same osmotic pressure, contain 224 gm. of sucrose. To bring the osmotic pressure up to 1 atmosphere, this weight of

sucrose must be increased to $\frac{224 \times 1}{0.66}$ gm., i.e. 340 gm.—which is in good agreement with the M.W. 342.

It follows from van't Hoff's work that *equal volumes of solutions exerting equal osmotic pressures at the same temperature contain equal numbers of solute molecules.*

These laws of osmotic pressure apply with reasonable accuracy to very dilute solutions only. The behaviour of less dilute solutions deviates widely from that calculated by their aid. As we shall see later, solutions of electrolytes also give abnormal values for osmotic pressure.

Examples: (i) Calculate the osmotic pressure, at 17°C. , of a solution of urea (M.W. 60) containing 2 gm. urea per litre.

60 gm. urea in 22.4 litres solution gives an O.P. of 1 atmosphere at 273°Abs.

\therefore 2 gm. urea in 22.4 litres solution gives an O.P. of $\frac{2}{60}$ atmospheres at 273°Abs.

\therefore 2 gm. urea in 1 litre solution gives an O.P. of $\frac{2 \times 22.4}{60}$ atmospheres at 273°Abs.

$$= \frac{2 \times 22.4 \times 290}{60 \times 273} \text{ atmospheres at } 290^\circ \text{Abs.}$$

$$= \underline{0.79 \text{ atmospheres.}}$$

(ii) Find the M.W. of glucose, given that a 3 per cent solution of this substance exerts an osmotic pressure of 3.9 atmospheres at 15°C.

22,400 c.c. of this solution contain 672 gm. glucose,

\therefore a solution exerting 1 atmosphere O.P. at 15°C. would contain $\frac{672}{3.9}$ gm. glucose.

At 0°C. $\frac{672}{3.9} \times \frac{288}{273}$ gm., i.e. 181 gm., would be required.

\therefore M.W. of glucose = 181.

Theory of Osmotic Pressure. In the experiment with the capillary tube described above on p. 150 the osmosis takes the form of a *distillation* from solvent to solution. This can happen only if *the vapour pressure over the solution is less than that over pure solvent*, a principle of which further use will be made in the succeeding sections.

If the vapour pressures were not unequal then distillation must occur at equal rates in each direction. Now the essential feature of all *osmometers*, i.e. apparatus for measuring osmotic pressure, is that they allow increased pressure to be imposed on the *solution* but prevent its application to the solvent: the interposition of a semi-permeable membrane is the means of confining the action to the solution. Such an arrangement is most obvious in Berkeley and Hartley's apparatus. The effect of this increase of pressure (called the osmotic pressure) is to arrest osmosis, and therefore *to raise the vapour pressure of the solution* until it is equal to that of the solvent; in other words, to bring solution and solvent into equilibrium.

We can understand how increase of pressure upon a liquid raises its vapour pressure as follows. Consider equilibrium between liquid and vapour to be established by bringing liquid into a vacuum space, and allowing it to evaporate. As always, equilibrium corresponds to a minimum free energy. If x is the last small fraction of a gram-molecule of liquid evaporating to reach the final equilibrium then (for reasons we have seen before):

$$\begin{aligned} & -x(\text{molar free energy of liquid}) \\ & +x(\text{molar free energy of vapour})=0, \\ \text{or } G_{\text{liquid}} &= G_{\text{vapour}}. \end{aligned}$$

But the molar free energy of the vapour at pressure p and temperature T is $RT \log p + \text{a constant}$ (see p. 126). Hence to increase vapour pressure at constant temperature the molar free energy of the *liquid* must be raised, and we saw on p. 126 (by means of the relation $dG = Vdp$) that this is the effect of imposing a pressure upon it.

It only remains to be noted that if we interpret osmotic pressure in this way and calculate its relation to concentration of solute and to temperature we arrive directly at the equation $\frac{P}{C} = RT$ for dilute solutions. It must therefore be emphasized that this relation (so admirably convenient for the purposes of calculations) does not justify any direct analogy between gas pressure and osmotic pressure. The cause of osmosis is that the molar free energy of solvent in a solution is always less, however dilute the solution, than the molar free energy of the pure solvent.

MOLECULAR WEIGHTS IN SOLUTION

Measurement of osmotic pressure is not the only method available for determining the molecular weight of a dissolved substance. Other methods, some of which are very simple to carry out in practice, will now be described.

Vapour Pressure of Solutions. The vapour pressure of a pure solvent is constant at constant temperature. The vapour pressure of the solvent in a solution is always lower than that of the pure solvent, and it can be shown from theoretical considerations as well as by experiment that the ratio $\frac{p-p'}{p}$ is equal to the *molar fraction* of solute $\frac{n}{N+n}$, when p is the vapour pressure of the solvent, p' is that of the solution, n is the number of gram-molecules of solute, and N is the number of gram-molecules of solvent.

For dilute solutions, n is negligible in comparison with N , so that the expression may then be simplified to:

$$\frac{p-p'}{p} = \frac{n}{N}$$

p and p' can be measured, and N can be calculated by dividing the weight, W , of solvent by its molecular weight, M . n is similarly $\frac{w}{m}$, where w is the weight of solute taken, and m is its molecular weight. Hence in the equation:

$$\frac{p-p'}{p} = \frac{\frac{w}{m}}{\frac{W}{M}} = \frac{wM}{Wm}$$

only m is unknown. Its value may thus be calculated from the experimental figures.

Though this method of determining molecular weights is seldom used, it can give good results if carried out carefully.

Examples: (i) The vapour pressure of ether at a certain temperature was found to be 720 mm. The vapour pressure of a solution of 2.7 gm. of a non-volatile substance in 100 gm. of ether was 702 mm. at the same temperature. Calculate the M.W. of the substance, given that the M.W. of ether is 74.

$$\frac{p-p'}{p} = \frac{720-702}{720} = \frac{18}{720}$$

$$\frac{wM}{Wm} = \frac{2.7 \times 74}{100 \times m}$$

$$\therefore \frac{18}{720} = \frac{2.7 \times 74}{100 m}$$

$$\therefore m = \underline{80.}$$

(ii) Calculate the vapour pressure of a 10 per cent solution of sucrose, $C_{12}H_{22}O_{11}$, at 98°C . M.W. of sucrose = 342. Vapour pressure of water at $98^\circ = 707 \text{ mm}$.

$$\frac{p-p'}{p} = \frac{n}{N} = \frac{\frac{10}{342}}{\frac{90}{18}}$$

$$\therefore \frac{707-p'}{707} = \frac{10 \times 18}{342 \times 90}$$

$$\therefore p' = \underline{703 \text{ mm.}}$$

Elevation of Boiling-point. Since a liquid boils when its vapour pressure becomes equal to the external pressure (normally 760 mm.), and since solutions have lower vapour pressures than the pure solvent at the same temperature, it follows that they must boil at

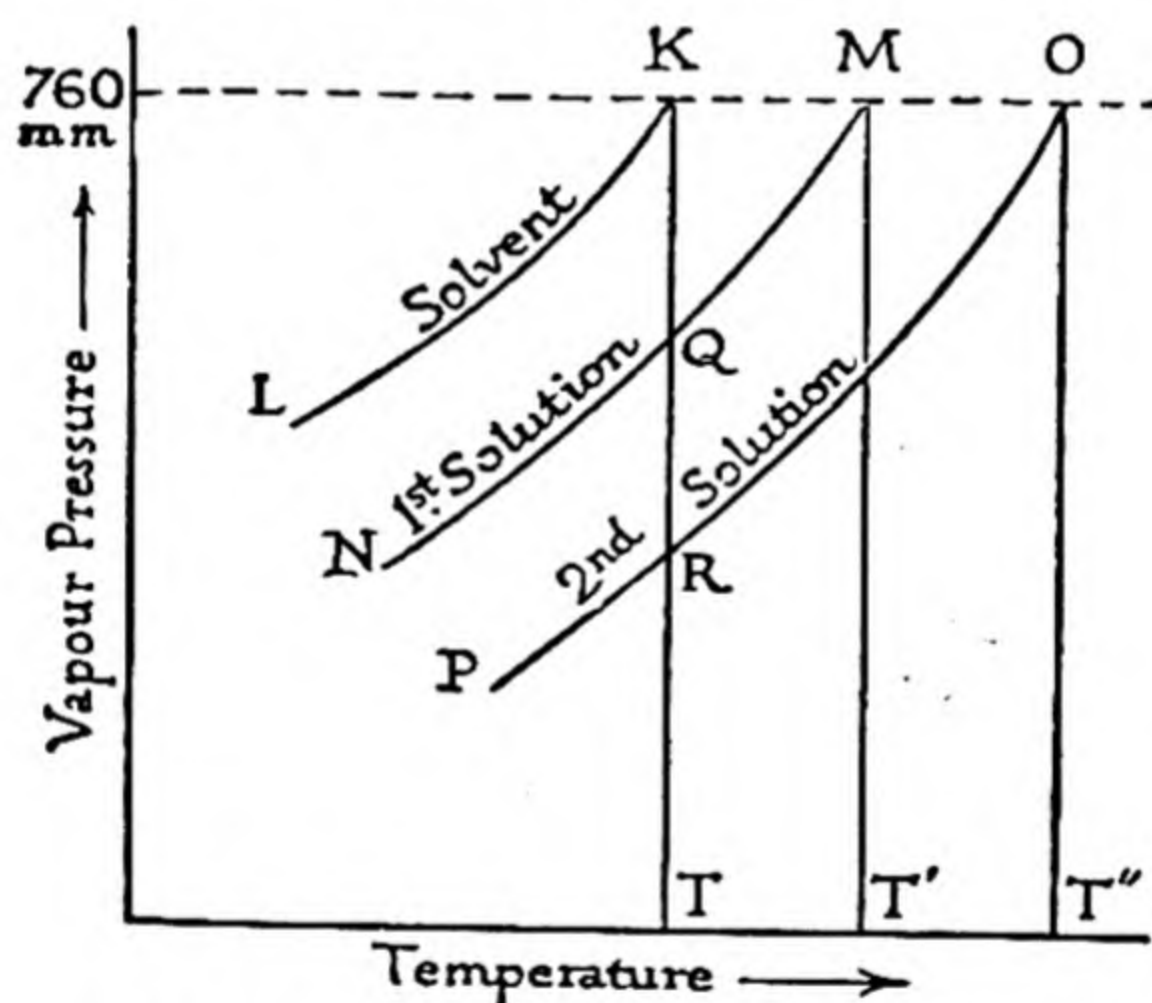


FIG. 38. V.P.—TEMPERATURE CURVES

higher temperatures. As shown in Fig. 38, curves (NM, PO) for the vapour pressure of dilute solutions of the same solvent and solute are almost parallel to one another and to the vapour pressure curve (LK) of the pure solvent. Hence by geometry:

$$KQ : KR :: KM : KO.$$

But KQ and KR represent the lowering of the vapour pressure

in the solutions, while KM and KO represent the amount by which boiling-points of the solutions (T' and T'') exceed that of the pure solvent (T). That is, the elevation of the boiling-point ($T' - T$) is a measure of the lowering of the vapour pressure $p - p'$. But in the expression

$$\frac{p - p'}{p} = \frac{wM}{Wm}$$

p and M are constants for a given solvent at its boiling-point.

$$\therefore k'(p - p') = T' - T = k \cdot \frac{w}{Wm}$$

When k has been determined for a suitable weight, A , of a particular solvent, this formula may be used to determine the molecular weight of a substance dissolved in the solvent; for, representing $T' - T$, found when w grams are dissolved in W grams of solvent, by t ,

$$m = \frac{k \cdot w \cdot A}{t \cdot W}$$

The values of the constant, k , for 100 gm. of various solvents, are as follows:

Solvent (100 gm.)	k
Water	5.2°
Alcohol	11.5°
Benzene	26.7°
Ether	21.0°
Chloroform	36.7°

These figures, then, represent the elevation of the boiling-point of the solvent caused by dissolving one gram-molecule of the solute in 100 gm. of the solvent. Actually, reliable results are obtained only in dilute solutions, and the above values were calculated from values determined in much less concentrated solutions.

In conducting a molecular-weight estimation by the boiling-point elevation, or *ebullioscopic*,* method, a suitable volume of the pure solvent is carefully boiled (to avoid superheating) and the boiling-point is noted. A known weight of the solute is introduced, and the boiling-point of the solution is found. For approximate work, the volume of the solution—which is contained in a graduated boiling-tube—is now read; this is taken to be the same as the volume of the solvent, and the weight of the latter is then calculated from its specific gravity. Details of the method are described in the practical textbooks.

* i.e. 'watching the boiling.'

Example: 0.754 gm. of a substance in 15 c.c. of alcohol gave a solution boiling at 78.80° . The boiling-point of alcohol was found to be 78.40° , and its specific gravity is 0.78. Find the M.W. of the substance, k for 100 gm. alcohol being 11.5° .

$$m = \frac{k.w.A}{t.W}$$

$$= \frac{11.5 \times 0.754 \times 100}{0.40 \times (15 \times 0.78)}$$

$$= 185.$$

Or, from first principles:

An elevation of 0.40° is given in 15×0.78 gm. alcohol by 0.754 gm. solute.

\therefore an elevation of 11.5° is given in 15×0.78 gm. alcohol by $\frac{0.754 \times 11.5}{0.40}$ gm. solute.

\therefore an elevation of 11.5° is given in 100 gm. alcohol by $\frac{0.754 \times 11.5 \times 100}{0.40 \times 15 \times 0.78}$
 $= 185$ gm. solute.

Depression of the Freezing-point. A pure solvent has a higher freezing-point than the solution made by dissolving a small quantity of solute in it, and it can be shown that (as with the elevation of the boiling-point) the depression of the freezing-point is a measure of the lowering of the vapour pressure. Hence a similar formula expresses the relationship between the molecular weight of the solute and the freezing-point depression produced when a known weight of it is dissolved in a known weight of solvent:

$$m = \frac{k.w.A}{t.W}.$$

The values of k are different from those of the boiling-point constants. Some are given below:

Solvent (100 gm.)	k
Water	18.6°
Acetic Acid	39.0°
Benzene	51.0°
Nitrobenzene	69.9°
Camphor	400°

The freezing-point or *cryoscopic** method of determining molecular weights of dissolved substances is extremely useful and very convenient. It was discovered empirically by RAOULT (1832-1901). The Englishman SIR CHARLES BLAGDEN (1748-1820) had found that—using the same solute and solvent—the depression of the freezing-point of the solvent was proportional to the concentration of the solution. In 1882, Raoult continued Blagden's work, and was able to show that *dilute equimolecular solutions in a given mass of the same solvent have the same freezing-point*.

As of the similar phenomena already described, this statement is true of *dilute* solutions only. The depressions produced in dilute solutions are, however, very small, and must be read to hundredths of a degree. For this purpose the special BECKMANN thermometer is used. It has a range of only some six degrees, but the actual temperatures of the range can be adjusted by altering the amount of mercury in the bulb. The freezing-point of the pure solvent, as shown on the suitably adjusted thermometer, is first determined, and the freezing-points of dilute solutions of the substance under investigation are subsequently found, using the same thermometer. The required *depressions* are therefore obtained, though the actual temperatures of the freezing-points are not known; they are, of course, unnecessary.

Since the value of k for 100 gm. camphor is so great (400) the depressions produced when this substance is used as solvent are very large, and may be determined with an ordinary thermometer graduated in degrees.

Examples: (i) 0.56 gm. of a substance in 15 gm. of water produced a depression of the freezing-point of 0.27° . k for 100 gm. water is 18.6. Find the M.W. of the substance.

$$\begin{aligned} m &= \frac{k.w.A}{t.W} \\ &= \frac{0.56 \times 18.6 \times 100}{0.27 \times 15} \\ &= \underline{257.} \end{aligned}$$

(ii) The freezing-point of camphor is 178° . A mixture of 0.72 gm. of a substance with 8.3 gm. camphor melted at 151° . k for 100 gm. camphor = 400. Calculate the M.W. of the substance.

* i.e. 'watching the ice.'

$$\begin{aligned}
 m &= \frac{k.w.A}{t.W} \\
 &= \frac{400 \times 0.72 \times 100.}{27 \times 8.3} \\
 &= \underline{129.}
 \end{aligned}$$

The Molecular Weights of High Polymers. This generation has seen the chemical synthesis of a vast range of fibres, such as rayon or nylon, of resins, such as bakelite, and of flexible or elastic materials such as polythene, cellophane, and the synthetic rubbers. The very large molecules composing these materials are the result of progressive chemical condensation or polymerization of relatively small molecules, and in their manufacture it becomes essential to control the degree of condensation; if stopped at a certain stage a desired flexible product may result, which is converted into a useless hard and brittle material by further condensation. For this purpose the determination of molecular weight is necessary.

Suppose that the molecular weight at the desired stage is 10,000. Then 20 gm. of the condensed material dissolved in 1,000 gm. of benzene, or 18 gm. in 1,000 c.c., gives a freezing-point depression of

$$\frac{20}{10,000} \times 5.1 = 0.010^{\circ},$$

which is barely measurable with accuracy. The osmotic pressure of the solution at 0° is approximately

$$\frac{18}{10,000} \times 22.4 \times 760 = 30.5 \text{ mm. of mercury,}$$

which is easily measured. Compact osmometers, in which cellophane or a similar material forms the membrane, are now commonplace instruments in the synthetic laboratory.

The laws of osmotic pressure stated on p. 153 are 'ideal' laws, exactly obeyed only at extreme dilution. If the relation $\frac{P}{C} = a \text{ constant}$ were true for a molar solution (one gm.-mol. of solute per 1,000 c.c., $C=1$) then at 0° C. the osmotic pressure of such a solution would be 22.4×760 mm. Hence for an extremely dilute solution at 0° C:

$$\frac{P}{C} = a \text{ constant} = 22.4 \times 760 \text{ (mm. mole).}$$

To find the molecular weight of a high polymer the osmotic pressures of a series of solutions containing m grams per litre are observed at a known temperature T , and the ratio $\frac{P}{m}$ is plotted

against m . The graph is projected to intersect with the $\frac{P}{m}$ axis. At the intersection the value of the ratio is given for vanishingly small concentration, where ideal conditions apply.

If M is the molecular weight sought,

$$\frac{P}{C} = \frac{P \times M}{m} = 22.4 \times \frac{T}{273} \times 760$$

$$\text{whence } M = \frac{\left(22.4 \times \frac{T}{273} \times 760\right)}{\frac{P}{m}} \quad (m \text{ very small})$$

Example: The osmotic pressures at 25° C. of solutions of a high polymer were found to be:

Gm. per 1,000 c.c.	50	75	100	125
Osmotic pressure (mm.)	7.1	11.0	15.5	21.0

Calculate the molecular weight of the polymer.

We find

$\frac{P}{m}$	0.142	0.147	0.155	0.168
m	50	75	100	125

On plotting $\frac{P}{m}$ against m the curve intersected the $\frac{P}{m}$ axis at the value 0.130.

$$\text{Hence } M = \frac{22.4 \times 760}{0.130} \times \frac{298}{273} = \underline{143,000}.$$

van't Hoff's Coefficient. van't Hoff and other chemists found that abnormal results for osmotic pressure and related effects—lowering of vapour pressure, elevation of boiling-point, and depression of freezing-point, of solutions—were given by electrolytes. A solution of common salt, for instance, showed nearly twice, and a dilute solution of barium chloride nearly three times, the freezing-point depression that was expected. Until this behaviour could be explained, van't Hoff proposed to use the coefficient i (*van't Hoff's coefficient*) to represent the factor by which the calculated result must be multiplied to give the actually observed result:

$$i = \frac{\text{observed result}}{\text{calculated result}}$$

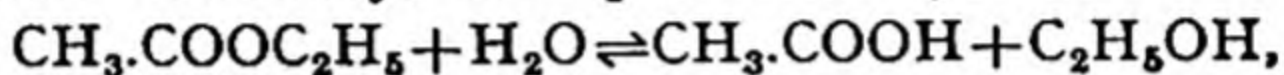
The significance of this coefficient will be seen in Chapter XVI.

CHAPTER XIII

THE PHASE RULE

Homogeneous and Heterogeneous Systems. In the study of chemical equilibrium, we have found two useful guides to be the law of mobile equilibrium (p. 128) and Le Chatelier's principle (p. 130). A third guide, all the more valuable because it is often able to provide information which the other two cannot, is the *Phase Rule* (1874-8) of WILLARD GIBBS.

A chemical system in equilibrium may be either homogeneous or heterogeneous, i.e. there may be no physical boundaries between any of its parts, or such a boundary or boundaries may exist. Thus, in the equilibrium $\text{N}_2\text{O}_4(\text{gas}) \rightleftharpoons 2\text{NO}_2$, both parts of the system are gaseous, and since all gases are completely miscible the system is homogeneous. Similarly, the equilibrium system



where the four substances—ethyl acetate, water, acetic acid, and ethyl alcohol—are all dissolved in one another to form a single liquid solution, is homogeneous. On the other hand, if liquid water and water-vapour are in equilibrium with one another at a fixed temperature and pressure, there is a definite boundary between the liquid and the gas, and the equilibrium is heterogeneous. Two immiscible liquids in equilibrium with one another form a heterogeneous system, and so do a solid and gas; two solids; a solid, liquid, and gas, etc.

These distinct, and mechanically separable, parts of a heterogeneous system are known as *phases*.* A phase need not consist of a single substance, though it may do so; but it must always be homogeneous. A mixture of gases, since it is always homogeneous, represents a single phase, and so does a homogeneous solution, e.g. a solution of copper sulphate. A saturated aqueous solution of copper sulphate, in contact with solid copper sulphate and in equilibrium with water-vapour, forms a system of three phases, viz. solid, liquid, and gas. A mixture of solids (unless it is a solid solution) is regarded as composed of as many phases as there are solids in it.

Components. Gibbs introduced the term *components*, and defined it as the smallest number of constituent substances in terms of

* This use of the word 'phase' has no relation to its other uses, as in wave-motion and so on.

which the composition of each phase in a system can be expressed in a chemical equation. A few examples will make this somewhat puzzling idea intelligible.

(i) Equilibrium system: $\text{Ice} \rightleftharpoons \text{water} \rightleftharpoons \text{water-vapour}$.

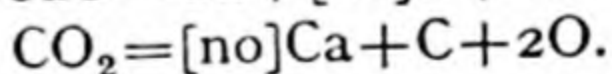
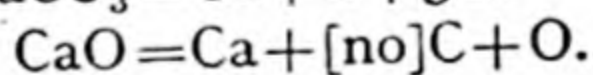
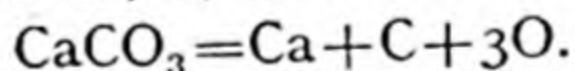
Each phase is composed of hydrogen and oxygen, but always in fixed proportions by weight: hence the composition of each phase is known by stating the weight in it of *either* hydrogen *or* oxygen—both weights are not required. Hence the number of *components* is 1. If free oxygen or hydrogen were added to the system the fixity of proportions would be destroyed, and the system would become one of *two* components.

(ii) Equilibrium system: $\text{Ammonium chloride} \rightleftharpoons \text{ammonia} + \text{hydrogen chloride}$.

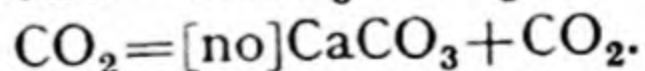
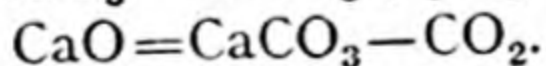
In this system there are two phases, solid and gaseous, and the whole is composed of the three elements, N, H, and Cl. The fact that the gaseous phase consists of partially (or wholly) dissociated ammonium chloride does not invalidate the statement that in all parts of this system the amounts of any two of the elements become fixed when the amount of the remaining element is stated. Hence the system has only *one* component. If excess of ammonia or hydrogen chloride were added, then all that could be said is that in the system as a whole, any *two* of the elements N, H, or Cl determine the proportion of the third: hence the system would have 2 components.

(iii) Equilibrium system: $\text{Calcium carbonate} \rightleftharpoons \text{calcium oxide} + \text{carbon dioxide}$.

If calcium carbonate is heated in a closed vessel, then at a constant temperature an equilibrium is set up between the carbonate, lime, CaO, and carbon dioxide. There are three phases, viz. the gas and the two solids. The composition of any phase could be expressed in terms of Ca, C, and O:



It may, however, also be expressed in terms of CaCO_3 and CO_2 :



It cannot be expressed in terms of one constituent only. Hence, since Ca, C, O = 3 constituents while CaCO_3 , CO_2 = 2 constituents, the number of *components* is 2. Another and briefer way of reaching this conclusion is to notice that while the system as a whole is

composed of the *three* species, Ca, C, and O, any *two* of these elements must chemically determine the third, in the system as a whole.

(iv) In deciding on the number of components in a system a too naïve view may often lead to erroneous results. Thus the system of the two salts, potassium nitrate, sodium chloride, with water, can be considered as composed of the five species, K^+ , Na^+ , Cl^- , NO_3^- and water. In the system as a whole electroneutrality demands that the cations K^+ and Na^+ *jointly* shall be equivalent to the anions Cl^- and NO_3^- , *jointly*, but this is the *only* restriction on the composition of the solid or liquid phases. The system therefore contains $5 - 1 = 4$ components. As this salt-water system can be formed by assembling only *three* compounds, viz. potassium nitrate, sodium chloride, and water, it might be thought that only *three* components are present. In general, the number of components is *the number of atomic (or ionic) species composing the system, less the number of independent chemical restrictions operating between them in all parts of the system.*

Degrees of Freedom. We may recollect that, according to Le Chatelier's principle, the application of constraint to a chemical system in equilibrium will cause a change to take place within the system tending to oppose the constraint and to restore the equilibrium. The most usual 'constraints' are (a) change of temperature, (b) change of pressure, and (c) change of concentration of one or more of the reacting substances.

If the application of any *one* of these constraints destroys the equilibrium of the system (in spite of the change tending to restore it), then the system is said to be *nonvariant* or to possess no *degrees of freedom*. If, however, the system succeeds in maintaining or restoring equilibrium when one (but not more) of the constraints is applied, it is said to be *univariant* or to possess 1 degree of freedom. Similarly, if the system is able to maintain or restore equilibrium when any *two* of the constraints are applied together, it is *bivariant*, possessing 2 degrees of freedom. Should all three constraints applied together fail to destroy equilibrium in the system, it is *tervariant* and has 3 degrees of freedom.

The Phase Rule. The phase rule discovered by Gibbs may now be given. It is:

For a system in equilibrium, the number of phases plus the number of degrees of freedom is equal to the number of components plus 2,

or

$$P + F = C + 2.$$

In order to understand the kind of problem with which the phase rule deals, it is simplest to refer to definite examples.

A Single Gaseous Phase. Here the three variables may be assumed to be temperature, pressure, and volume.

$$P=1 \text{ and } C=1.$$

$$P+F=C+2.$$

$$\therefore 1+F=3,$$

$$\therefore F=2.$$

There are thus 2 degrees of freedom, i.e. we can make a given mass of the gas occupy any desired *volume* at any desired *temperature*, but then the pressure will fix itself; or we can make the gas occupy any desired *volume* at any desired *pressure*, but if we do this we cannot also arbitrarily choose the temperature; or, finally, we are free to have the gas at any desired *temperature* and any desired *pressure*, but fixing these two variables means that the volume cannot also be arbitrarily settled. If we have 100 c.c. gas at N.T.P., we can decide to raise its temperature to 15°C . and its pressure to 77 mm., for instance, but we cannot also demand that the volume shall be 2 c.c., 3 c.c., or 1,000 c.c. The volume will indeed fix itself, at $\frac{100 \times 288 \times 760}{273 \times 770}$ c.c.

Water and Water-vapour. If water is in equilibrium with water-vapour, then $P=2$ and $C=1$.

$$P+F=C+2,$$

$$\therefore 2+F=3,$$

$$\therefore F=1.$$

There is 1 degree of freedom, and the system is univariant. If, then, we alter the temperature, the pressure will alter itself; or if we wish the pressure to be of a certain magnitude, we cannot also fix any temperature we like for this magnitude to be attained. Putting the same facts in another way, we may say that, at a constant temperature, water-vapour in contact with liquid water exerts a constant pressure.

Water and Ethanol with Vapour. This is a system of two components in two phases, since water and ethanol mix in all proportions.

$$P+F=C+2$$

$$\therefore 2+F=2+2$$

$$\therefore F=2$$

The system is accordingly bivariant. Hence a given temperature and a given pressure fix the composition of the liquid phase and of the vapour above it. If only a pressure is specified, numerous liquid mixtures, of differing composition, could, at particular temperatures, develop this pressure. The vapour pressure of a

mixture of given composition is fixed by specifying its temperature. If any two of the conditions, pressure, temperature, and composition, are given then the third is automatically fixed.

Ice, Water, and Water-vapour. Here there are 3 phases and 1 component.

$$\begin{aligned} P + F &= C + 2, \\ \therefore 3 + F &= 3, \\ \therefore F &= 0. \end{aligned}$$

This system has no degrees of freedom; it is nonvariant. If, therefore, ice, water, and water-vapour are to exist in equilibrium with one another, it can be at only one particular temperature and pressure, which the system will fix for itself. Neither the temperature nor the pressure can be chosen, or altered, at our own fancy.

The actual temperature and pressure at which the system is in equilibrium are 0.0076° and 4.5 mm. This is known as the *triple point* for water. The reader may wonder why the temperature is 0.0076° , when he has probably learned that ice and water are in equilibrium at 0.0000° . The explanation is that ice and water are in equilibrium at 0.0000° in the absence of water-vapour and at a pressure of 760 mm. At equilibrium between ice, water, and water-vapour, the pressure of the latter proves to be 4.5 mm.; now the melting-point of ice is raised by lowering of pressure (by Le Chatelier's principle, for ice contracts on melting), and the decrease of pressure from 760 mm. to 4.5 mm. is sufficient to raise the melting-point from 0.0000° to 0.0076° .

Phase Rule Diagram for Water. The facts just considered, with others relevant to the subject, may be expressed graphically in the form of a diagram. In Fig. 39, which is *not* drawn to scale, the curves have been distorted in order to explain more clearly some of the important points.

OB is the line which shows the kind of way in which the melting-point of ice is affected by change of pressure. It indicates that, with increase of pressure, the melting-point is lowered, though a large increase in pressure causes only a small depression. (Even that shown in the figure is far larger than it would be if the figure were to scale.) If ice and water are to exist in equilibrium with one another, the temperature and pressure must be such that, when plotted on the diagram, they form one of the points composing OB.

The line OC is the vapour-pressure curve for water; i.e. it shows the various temperatures and pressures at which liquid and gaseous water can exist in equilibrium together. OD, a prolongation of OC, is the vapour-pressure curve of undercooled water, i.e. water which has been cooled to below its freezing-point without freezing.

Since an undercooled liquid is unstable, and solidifies when a crystal of its own solid form is introduced into it, OD is shown as a dotted line.

The line OA is the vapour-pressure curve of ice (in the absence of liquid water); it is sometimes known as the hoar-frost line. That solid ice has a vapour pressure at and below the melting-point is shown, for example, by the fact that ice and snow may gradually vanish from frozen roads without melting.

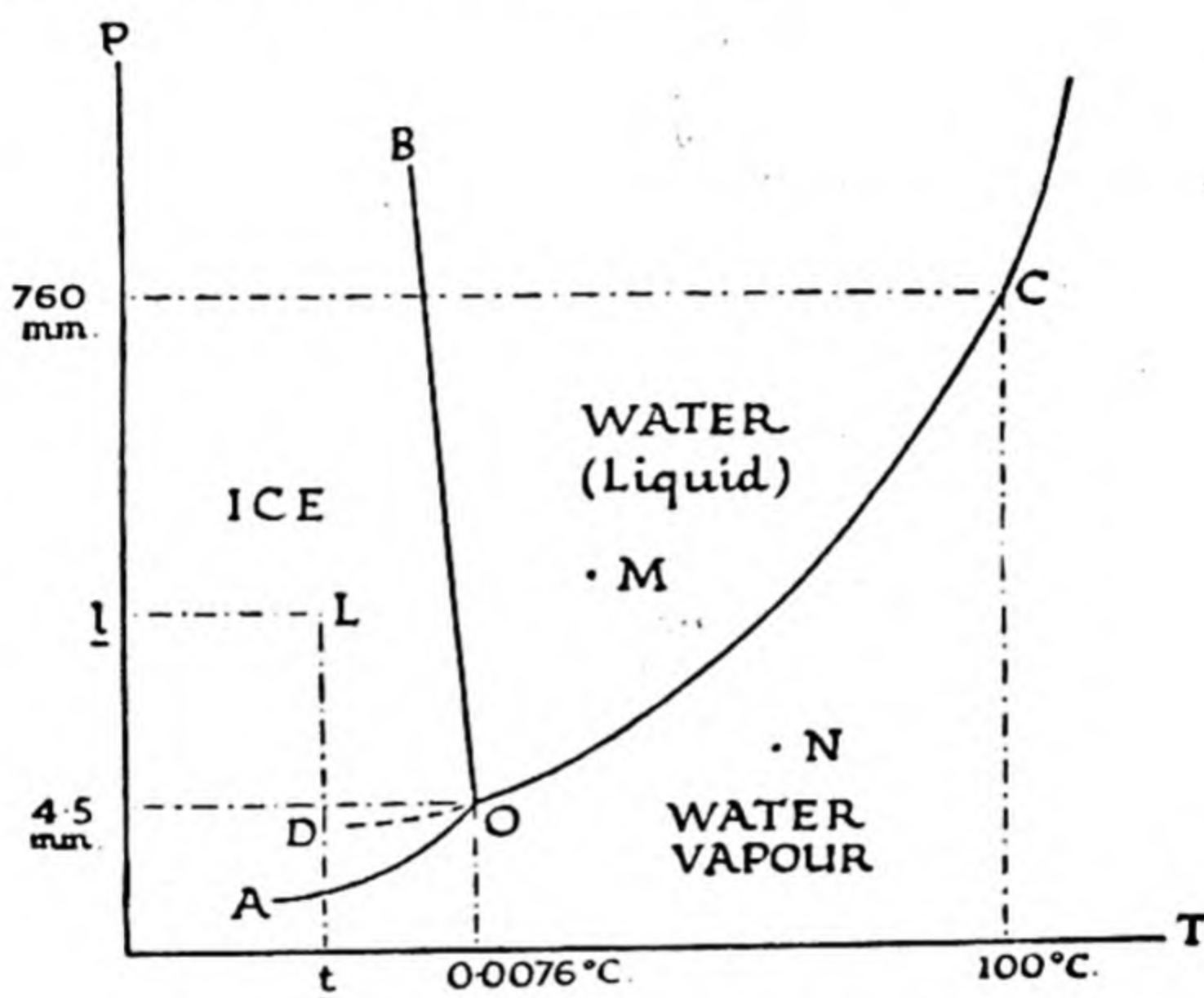


FIG. 39. PHASE RULE DIAGRAM FOR WATER
(DISTORTED AND NOT TO SCALE)

At O, ice, liquid water, and water-vapour can exist in equilibrium with one another. This, then, is the triple point; it marks the *only* conditions under which this triple equilibrium is possible.

Let us now investigate the conditions represented by points L, M, and N on the diagram. At L, the temperature is lower than that at which ice can exist in equilibrium with water at the corresponding pressure (l); and the pressure is higher than that at which water-vapour can exist in equilibrium with ice at that temperature (l). Hence under these conditions only ice can exist, and the same is true of any point in the area bounded by AO and OB.

In the area BOC only liquid water can exist. For, considering point M, we see that, at the pressure shown, the temperature is too high for the water to coexist stably with ice, and too low for it to

coexist stably with water-vapour. Similarly, in the area in which N is marked, only vapour can exist, for, at the temperature shown, the pressure is less than that at which vapour and water can co-exist.

Sulphur. There are many allotropic forms of sulphur (p. 517), but for the present purpose we may limit ourselves to a discussion of the equilibria possible between sulphur vapour, liquid sulphur, and the two common allotropes rhombic (or α) sulphur and monoclinic (or β) sulphur. It is well known that, at ordinary temperatures, monoclinic sulphur is unstable, gradually changing into the rhombic form. At temperatures above 95.6° , however, the position is reversed, rhombic sulphur then gradually changing into monoclinic sulphur. When maintained at 95.6° , neither form shows any tendency to pass into the other, and this temperature is known as the *transition point*.

Applying the phase rule, what are the conditions under which all four phases—vapour, liquid, rhombic, and monoclinic—could exist together in equilibrium?

$$\begin{aligned} P + F &= C + 2, \\ \therefore 4 + F &= 1 + 2, \\ \text{or } F &= -1. \end{aligned}$$

But a 'negative degree of freedom' is a mere contradiction in terms; what the phase rule indicates here is that *the four phases cannot be in equilibrium with one another under any conditions whatever*.

It seems probable, then, from the behaviour of water—where three phases gave one triple point—that the phase rule diagram for sulphur should show 3 triple points, viz. those between (i) rhombic, monoclinic, and vapour, (ii) rhombic, monoclinic, and liquid, (iii) liquid, vapour, and either rhombic or monoclinic according to which happens to be stable at the temperature concerned. From Fig. 40, it will be seen that this forecast is verified (though the dotted lines show a fourth triple point, C, which will be discussed in due course).

In the figure, PB is the vapour-pressure curve of rhombic sulphur; its continuation BC is possible since if rhombic sulphur is heated *rapidly* it does not change into monoclinic sulphur at 95.6° , but retains its solid form up to $113-14^\circ$, when it melts.

BD is the vapour-pressure curve of monoclinic sulphur, and B is the triple point between rhombic, monoclinic, and vapour. The conditions at this point are a temperature of 95.6° and a vapour pressure of 0.006 mm. Should there be no vapour phase, the transition temperature can be varied by varying the pressure, since there is now 1 degree of freedom ($C=1$, $P=2$, $\therefore F=1$).

DA shows the effect of pressure upon the melting-point of mono-

clinic sulphur, and D is the triple point between monoclinic, liquid, and vapour ($T=120^{\circ}$, $P=0.04$ mm.).

C is the triple point between rhombic, liquid, and vapour. It is shown as the meeting-point of three *dotted* lines because, within the triangular space ABD, the *stable* form is monoclinic. This is gradually formed from any or all of the other three phases within these limits.

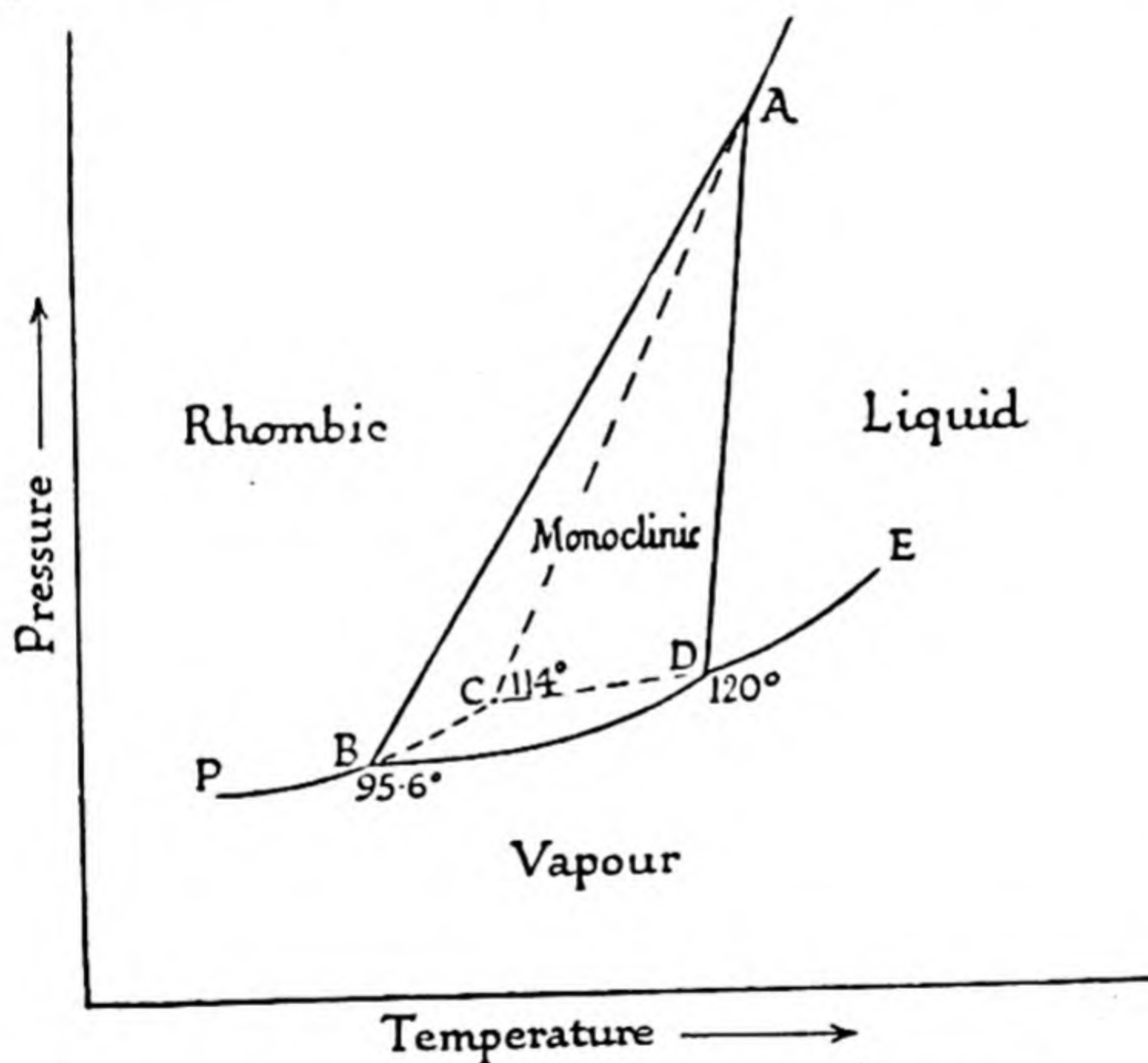


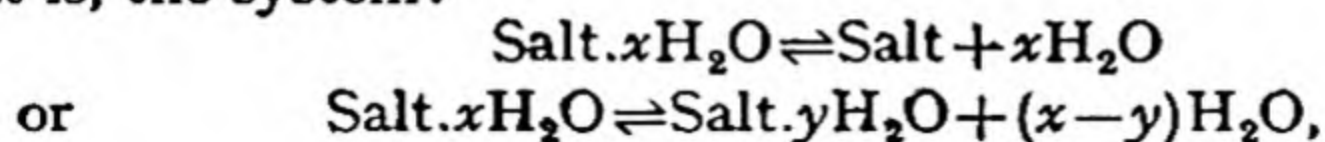
FIG. 40. PHASE RULE DIAGRAM FOR SULPHUR
(DISTORTED AND NOT TO SCALE)

A is the triple point between rhombic, monoclinic, and liquid. The conditions are stated to be $T=151^{\circ}$, $P=1,288$ atmospheres.

DE is the boiling-point curve, i.e. the vapour-pressure curve of liquid sulphur, while CD is the vapour-pressure curve of the unstable undercooled liquid sulphur made by rapidly heating rhombic sulphur to its melting-point. CA shows the effect of pressure upon the melting-point of rhombic sulphur.

Crystalline Hydrates. Crystalline hydrates, such as ferrous sulphate heptahydrate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, have a vapour pressure which, for a particular hydrate, is constant at constant temperature.

That is, the system:



is a two-component system consisting of three phases and possesses 1 degree of freedom.

Whether the salt decomposes direct into anhydrous salt and water-vapour on dehydration, or whether it forms an intermediate hydrate (or hydrates), can be discovered as follows. The hydrate is heated at a suitable temperature in a vessel provided with a manometer and a means of withdrawing water-vapour. If a little water-vapour is removed, the pressure will return to its original value if time is allowed for the equilibrium to establish itself. Finally, however, a point may be reached when removal of water-vapour brings the pressure steadily down to zero. In this case, the system was univariant as long as the pressure remained constant, and there were therefore three phases. The steady subsequent fall indicates a bivariant system and thus two phases, viz. anhydrous salt and water-vapour, all the hydrate having been decomposed.

If an intermediate hydrate is formed, the pressure will remain constant for a time (after re-establishment) as before, but will then fall to a *new* constant level, indicating the formation of a new three-phase system. The original three-phase system must therefore have been composed of water-vapour, the original hydrate, and a *second hydrate*. The number of new constant vapour-pressure levels reached on successive dehydration thus represents the number of intermediate hydrates formed.

Efflorescence and Deliquescence. If the vapour pressure of a hydrate exposed to the air is greater than the partial pressure of water-vapour in the atmosphere, it is clear that no equilibrium can be reached. The atmosphere will, in fact, act as an enormous desiccator, and the hydrate will lose water until it forms either a hydrate with a lower vapour pressure, or the anhydrous salt. In doing so, it loses its crystalline form and is said to 'effloresce.'

A solid 'deliquesces' if the vapour pressure of its *saturated solution* is less than the partial pressure of water-vapour in the air. Efflorescence is thus commonly a property of highly hydrated salts, such as $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, while deliquescence can only be shown by compounds very soluble in water, such as CaCl_2 , P_4O_{10} , or KOH .

Eutectic Systems. Eutectic systems have been briefly considered earlier, in connection with aqueous salt solutions (p. 141). Here we may show how the phase rule can be applied to predict the existence and behaviour of such a system. A single salt and water constitute a system of two components; hence $P + F = 4$, and four

co-existent phases are required for non-variance, while three such phases provide a univariant system. If therefore we choose to study a eutectic system under a fixed pressure, say atmospheric, three co-existent phases form a system of fixed properties, which will, however, undergo some change if the pressure is altered. Now the vapour pressure of salt solutions in the neighbourhood of their eutectic (or cryohydric) points is much less than one atmosphere, and by the choice of this pressure we in fact study the system in the absence of a vapour phase. Hence the system of three phases with fixed properties can only be *ice, salt, and solution*. Under atmospheric pressure therefore this system can exist at only one temperature—the eutectic temperature. In principle this temperature will be affected by a change of pressure, but the effect of moderate changes upon the properties of solids and liquids is so slight that the eutectic temperature may be regarded as constant for practical purposes. As shown in the diagrams studied in the preceding sections, the eutectic point, which is non-variant in our constant pressure system, is necessarily a point of intersection of the lines representing the two univariant systems derivable from it, viz. ice, solution and salt, solution—the ‘freezing-point line’ and the ‘solubility line.’ The former depicts equilibrium between ice and increasingly dilute solutions, terminating at 0° in the melting-point of ice: the other the solubility curve of the salt. It is interesting that the phase rule, by demanding that the solid at the eutectic point consist of *two* phases, discredits the former idea that this solid is a single ‘cryohydrate’ (p. 141).

CHAPTER XIV

THE RATE OF CHEMICAL REACTION

The Law of Mass Action. Two molecules of the substances A and B can interact with each other chemically only when they are in contact, i.e. in collision. It follows that whether A and B form a gaseous mixture or are dissolved in a solvent the number of pairs of molecules interacting in unit volume in unit time must be *proportional* to their *collision frequency*, the number of collisions made in unit volume in unit time. In Chapter VI on p. 58 a simple calculation was made of the number of collisions Z per c.c. per second in oxygen at N.T.P. The method of calculation could be expressed as

$$Z = \frac{n}{2} \times \frac{u}{l},$$

n = number of molecules per c.c. = *concentration*,

u = average speed of molecules,

l = distance between collisions = *the mean free path*.

Suppose now we consider oxygen not at N.T.P. but at 0° and under 2 atmospheres pressure: n will be replaced by $2n$, and l by $\frac{l}{2}$, and Z will be *quadrupled*. We deduce that in general

$$Z_A = \text{a constant} \times [A]^2$$

The collision frequency Z_{AB} for collisions between unlike molecules A and B must reduce to the above relation when A and B are the same. Hence

$$Z_{AB} = \text{a constant} \times [A].[B].$$

Therefore

$$\begin{aligned} \text{Rate of chemical action} &= \text{a constant} \times Z_{AB} \\ &= \text{a constant} \times [A].[B]; \end{aligned}$$

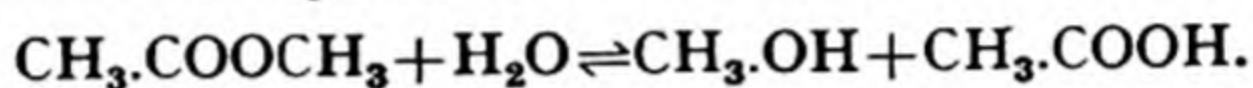
in words, *the rate of chemical reaction between A and B is proportional to the product of their concentrations.*

Guldberg and Waage's Enunciation. The importance of concentration as affecting the rate of a chemical change was perceived by BERTHOLLET in 1799, but an attempt to express the quantitative aspect was first made by GULDBERG and WAAGE, two Norwegian scientists, in 1867. As a result of their own and other investigations,

they were able to state the following law, which is known either after its discoverers or as the 'Law of Mass Action':

The rate at which a substance reacts is proportional to its active mass; and the rate of a chemical reaction is proportional to the product of the active masses of the reactants. It appears strange to-day that the authors of this law should have chosen the abstruse term 'active mass,' especially as they themselves explained in their exposition of the law that 'active mass' was synonymous with molecular concentration. It may well be that they were cautious of the latter term at a time when the long period of scepticism and distrust about molecular weights had been so recently ended by the efforts of Cannizzaro (p. 27).

Verification of the Law of Mass Action. (1) *Hydrolysis of Methyl Acetate.* When methyl acetate is heated with water, it is slowly hydrolysed into methyl alcohol and acetic acid:



The rate of hydrolysis is greatly increased by the addition of a small amount of dilute hydrochloric acid (which acts as a catalyst) and is then conveniently measurable at a temperature of 25° – 30° .

According to the law of mass action, the rate of hydrolysis at any given moment is proportional to the product of the concentrations of methyl acetate and water at that moment, and is equal to this product multiplied by a constant, k . If a large excess of water is used, its concentration will change but little, and may be regarded as constant. Hence the rate of hydrolysis should be proportional to the concentration of the methyl acetate, or

$$\frac{[\text{CH}_3\text{COOCH}_3]}{\text{Rate of hydrolysis}} = \text{a constant}.$$

When 100 ml. of N/2 hydrochloric acid, contained in a flask immersed in a thermostat at 25° have assumed that temperature, 5 ml. of methyl acetate are dissolved in the acid, and portions of the liquid are removed at timed intervals and titrated with standard alkali. The titration readings give a measurement of the rate of hydrolysis, since acetic acid is formed as one of the products; hence the difference between two successive titrations is a measure of the methyl acetate hydrolysed during the interval.

The weights of methyl acetate hydrolysed are now plotted against the times, and a curve similar to that shown at AB in Fig. 41 is obtained.

Taking the two points P and P', the average rate of hydrolysis over the period of time represented by PQ is $\frac{P'Q}{PQ}$. If P and P' are

brought closer and closer together, this ratio becomes equal to $\frac{RQ}{PQ}$, i.e. to the tangent of the angle θ (\hat{RPQ}).

Hence *rate of reaction at P* = $\tan \theta$.

By drawing tangents at several different points, a series of values may be obtained for $\tan \theta$, and when these are plotted against the

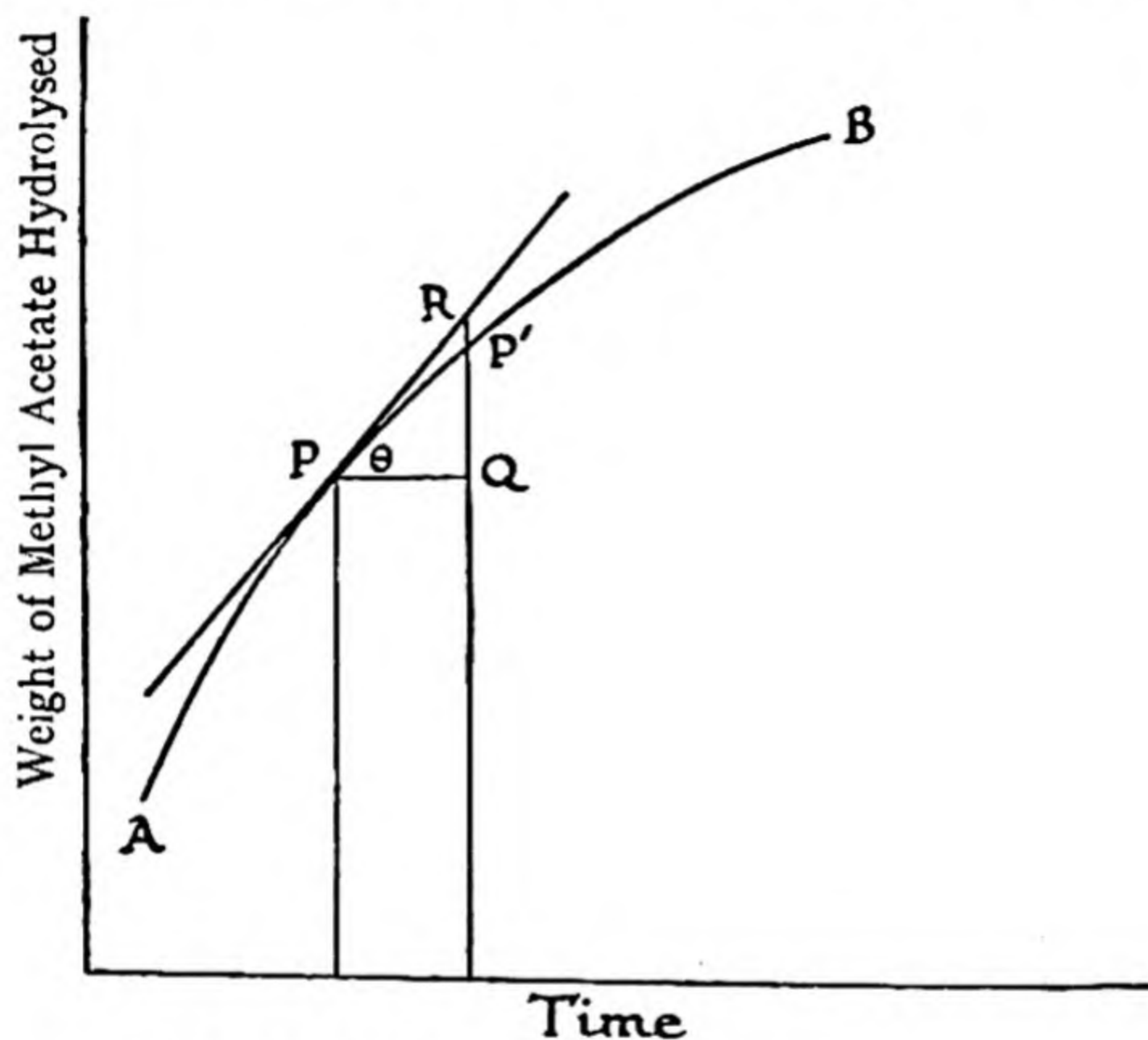
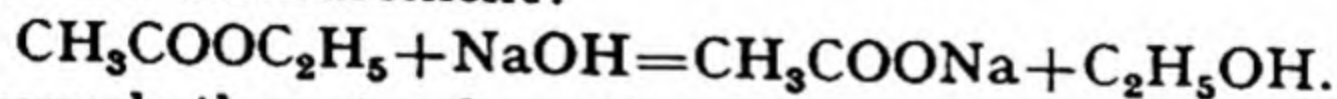


FIG. 41. HYDROLYSIS OF METHYL ACETATE

corresponding values for the weights of methyl acetate remaining unhydrolysed, a straight line is obtained. Therefore

$$\text{rate of hydrolysis} = [\text{methyl acetate}] \times \text{a constant.}$$

(2) *The Saponification of Ethyl Acetate* (Warder, 1881). At about 25° ethyl acetate is decomposed by dilute aqueous alkalis at a rate convenient for measurement:



In this example the rate of reaction should be given by:

$$\text{Rate} = k \times [\text{ethyl acetate}] [\text{alkali}].$$

The results of experiments are very easily computed if equimolecular

quantities of ethyl acetate (M.W. 88) and alkali are contained in the original solution, for then the molecular equivalency will be maintained throughout the course of the reaction:

$$\text{Rate} = k [\text{ethyl acetate}]^2 = k [\text{alkali}]^2.$$

It will be seen that in a reaction of the type $A + B = C + D$:

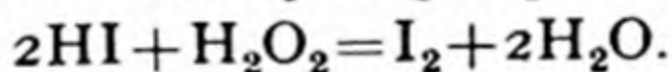
$$\begin{aligned} \text{Rate of reaction} &= \text{Rate of decrease of } [A] \text{ or } [B] \\ &= \text{Rate of increase of } [C] \text{ or } [D], \end{aligned}$$

and this remains true whatever the initial molecular relation of the reactants. Hence in measuring the rate of reaction experimentally any of the four concentrations may be chosen for estimation, depending on convenience.

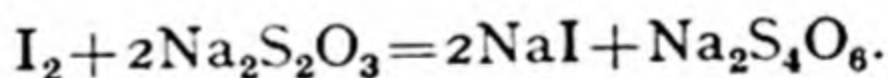
After standing separately in the thermostat to assume its temperature, 100 ml. of an aqueous solution containing 0.44 gm. of ethyl acetate and an equal volume of N/20 sodium hydroxide are mixed. Portions of the mixture (10 ml.) are removed at timed intervals, and their content of alkali estimated by titration. A figure similar to Fig. 41 is plotted and the result deduced that

$$\frac{[\text{Ethyl acetate}]^2}{\text{Rate of saponification}} = \text{a constant.}$$

(3) *The Experiments of Harcourt and Esson* (1866-7). These chemists studied the rate of the reaction in aqueous solution between hydrogen iodide and hydrogen peroxide:



They adopted a very ingenious method of timing the rate of production of iodine, based on its reconversion to iodide by sodium thiosulphate:



To one litre of a solution containing a large excess of potassium iodide acidified with sulphuric acid together with a few ml. of aqueous starch solution, 10 ml. of a dilute solution of hydrogen peroxide are added. Almost at once the well-known blue starch-iodine colour develops in the solution, but the addition of 5 ml. of a dilute solution of thiosulphate restores the colourless condition. After a timed interval the blue colour suddenly reappears and is once more removed by adding a further 5 ml. of thiosulphate solution, and so on. The timed intervals between addition of portions of thiosulphate steadily lengthen, since they represent the rate of production of a fixed amount of iodine (equivalent to 5 ml. of the thiosulphate solution) by a diminishing concentration of hydrogen peroxide. By this means the relation

$$\text{Rate of production of iodine} = k. [\text{H}_2\text{O}_2]$$

was established.

The influence on the reaction rate of hydrogen iodide concentration can be found if some of the potassium iodide in the original solution is replaced by its equivalent of potassium chloride (hydrochloric acid is not affected by hydrogen peroxide in dilute solution): after such replacement the concentration of iodide can still be in sufficient excess to remain nearly constant during reaction with the peroxide. For example, when the concentration is reduced to two-thirds by this means, the rate falls to two-thirds of its original value. It follows that for the whole reaction the rate is expressible as:

$$\text{Rate} = k' \cdot [\text{H}_2\text{O}_2][\text{HI}]. \quad (\text{See p. 180})$$

The Velocity Constant. The constant (symbol k) appearing in expressions embodying the law of mass action is termed the *velocity constant* (or *coefficient*) of the reaction concerned. The rate of reaction of most reactions is conveniently stated as the *change of molecular concentration* (gm.-mol. litre⁻¹) in one *minute*: its units are therefore litre⁻¹.minute⁻¹. For a reaction of the type

$$\text{Rate (litre}^{-1}\text{.min.}^{-1}\text{)} = k \cdot X \cdot (\text{litre}^{-1}),$$

such as the hydrolysis of methyl acetate, the unit of k is evidently min.⁻¹ and for the type

$$\text{Rate (litre}^{-1}\text{.min.}^{-1}\text{)} = k \cdot XY \cdot (\text{litre}^{-2}),$$

such as the saponification of ethyl acetate, the units of k are litre.min.⁻¹. The velocity constant is never a mere number, although often erroneously stated as such.

The constant for the saponification of ethyl acetate by sodium hydroxide at 20° is 3.78 litre/min. This means that, for every litre of a solution containing 0.1 gm.-mol. (8.8 gm.) of ethyl acetate and 0.1 G.F.W. (4.0 gm.) of sodium hydroxide, $3.78 \times (0.10)^2 = 0.0378$ gm.-mol. (3.3 gm.) of ethyl acetate, and 0.0378 G.F.W. (1.51 gm.) of alkali must be steadily added per minute to balance loss by chemical action.

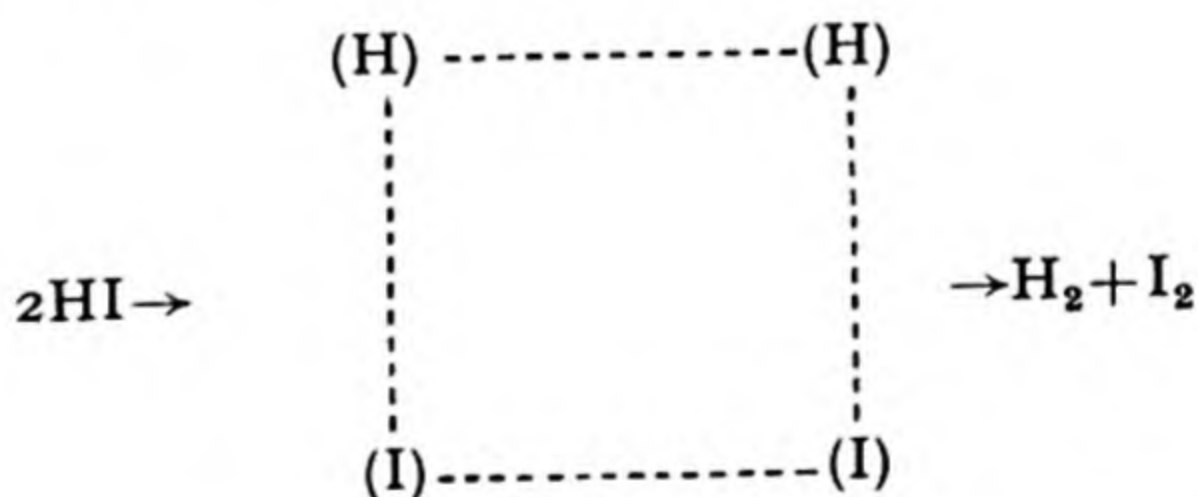
The velocity constant of almost every known reaction increases very rapidly with rise of temperature, usually by factors of 2—4 for a change of 10°. The efficiency of the domestic refrigerator in preserving foodstuffs from the reactions of fermentation and putrefaction depends on this sensitiveness of reaction velocity to even small changes of temperature.

Activation in Collisions. We now consider the actual events during a binary collision in which a chemical change occurs. In Chapter X, p. 116, a chemical change was regarded, from a thermochemical angle, as 'an always endothermic process of rupturing

bonds in reactants, followed by the always exothermic process of forming bonds in the products.' Such a view, while leading in the light of Hess's Law to a correct evaluation of heat of reaction, does not necessarily afford a picture of an actuality. If molecules were 'atomized' during chemical action the products would not consist only of a small and definite number of specific compounds, but of all those that could be formed by the totality of atoms concerned.

Energy acquired by a molecule (in definite quanta) does not all serve to increase its energy of movement ($\frac{1}{2}mu^2$), but a part goes to increase its *internal* energy, energy of *rotation*, and of *vibration*. It is the vibrational energy which is concerned in chemical change. It was explained in Chapter X, p. 106, for the case of a hydrogen molecule that in its normal state extension of the distance between atoms is opposed by attractive forces, and compression by repulsive forces, and this is the condition favouring vibrational motions. The energy and amplitude of such motions increase by definite quanta, and therefore through specific energy levels, until finally, if the molecule acquires sufficient energy, the amplitude becomes great enough to separate the atoms and the molecule dissociates.

Suppose now that two molecules of hydrogen iodide are in collision and have each by some means gained enough quanta of energy to excite them to a higher vibrational level but not to the final level of decomposition.



In the diagram amplitudes are indicated by dotted lines. It will be seen that a similar configuration would result by exciting a molecule of hydrogen and a molecule of iodine to their higher vibrational levels: indeed the system formed originally from hydrogen iodide could pass spontaneously into an excited molecule of hydrogen and another of iodine. If the change is to be stabilized the excess must be rapidly withdrawn from the new molecules, but in a gaseous system this is readily accomplished in the numerous impacts of surrounding molecules.

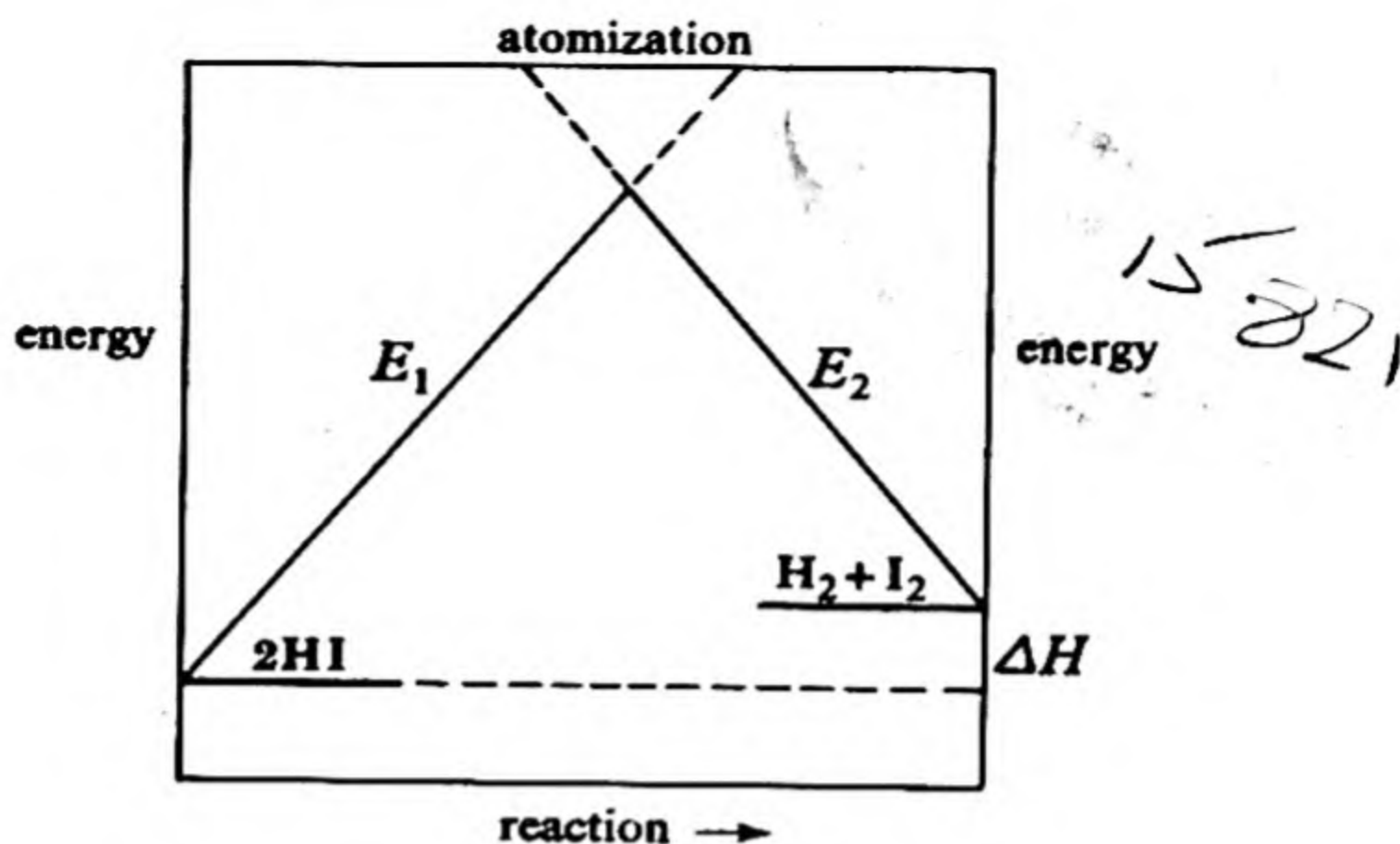


FIG. 42

Fig. 42 depicts the energy changes concerned in the course of the reaction. ΔH is the heat of reaction, E_1 and E_2 are termed the *energies of activation* for the changes $2HI \rightarrow H_2 + I_2$ and $H_2 + I_2 \rightarrow 2HI$ respectively. These energies are as follows:

$$E_1 = 43.8 \text{ kcal./gm.-mol.}$$

$$E_2 = 38.8 \text{ kcal./gm.-mol.}$$

$$\Delta H = 5.0 \text{ kcal./gm.-mol.}$$

Energy of Activation. Two observations provide the clue to the source of the activation energy:

(1) All velocity constants increase very rapidly with rise of the temperature of reaction.

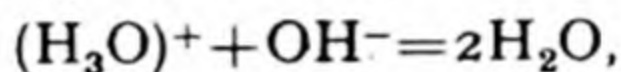
(2) The extreme scarcity of collisions resulting in chemical action.

At 400° the velocity constant for the reaction $2HI \rightarrow H_2 + I_2$ is found to be 1.32×10^{-3} litre/min. From this the number of molecules of hydrogen iodide decomposing per litre per minute is easily calculated, and half this number is the number of (binary) collisions effective at 400° and occurring in one litre during one minute. On the other hand, the methods of the kinetic theory give the *total* number of collisions (per litre per minute) at 400° . Comparing the two estimates we find:

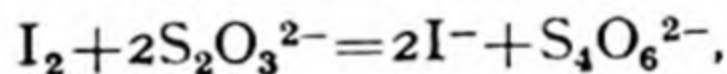
$$\frac{\text{Effective collisions}}{\text{Total collisions}} = 10^{-12}.$$

In assemblies of molecules, as in populations of living beings, deviations from a mean are scarce, and the scarcer the larger the deviation—giants and dwarfs are equally uncommon. Now the *mean* total energy per gram-molecule of hydrogen iodide at 400° is only about 5 kcal: the number of molecules with energy (per gm.-mol.) at least four times greater (half the activation energy per two molecules) will be almost vanishingly small. Detailed calculation shows the satisfactory agreement that their number is such as to give the ratio effective collisions/total collisions the required value (10^{-12}). The *average* or mean molecular energy rises in proportion to absolute temperature, but the fraction of highly excited molecules increases very much faster, and we can thus account for the rapid increase of velocity constant with temperature rise.

Fast Reactions. In reactions in solution between oppositely charged ions, familiar in quantitative and qualitative analysis, we have experience of the very high rates of reaction consequent upon high collisional efficiency. In neutralization of an alkali by a 'mineral' acid such as hydrochloric, the essential reaction is:

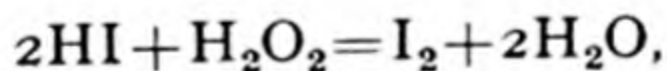


that is the transfer of a proton from the 'hydrogen' ion to the hydroxyl ion, which probably happens in a large proportion of collisions, if not in all. Reactions due to *electron* transfer, such as that between iodine and sodium thiosulphate:



are commonly also very fast.

Stages in Chemical Reactions. Harcourt and Esson's investigations of the rate of the reaction between hydriodic acid and hydrogen peroxide,



led conclusively to the result:

$$\text{Rate} = k. [\text{H}_2\text{O}_2][\text{HI}] \quad (\text{p. 177}).$$

Since the reactants could be written $\text{HI} + \text{HI} + \text{H}_2\text{O}_2$ an application of the law of mass action appears to require:

$$\text{Rate} = k. [\text{H}_2\text{O}_2][\text{HI}]^2.$$

A later study was conducted after the ionic theory had been fully accepted, and it was known that hydriodic acid is a strong electrolyte fully ionized in aqueous solution, while the degree of ionization of hypoiodous acid, HIO , is quite negligible in a solution which contains an excess of hydrogen ions. This investigation revealed that the reaction proceeds in several successive stages:

- (1) $\text{I}^- + \text{H}_2\text{O}_2 = \text{IO}^- + \text{H}_2\text{O},$
- (2) $\text{H}^+ + \text{IO}^- = \text{HIO},$
- (3) $\text{I}^- + \text{HIO} = \text{I}_2 + \text{OH}^-,$
- (4) $\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}.$

Now (2) and (4), involving oppositely charged ions, are practically instantaneous, while (3) is also very fast, so that iodine and water are formed at the same rate as the anion IO^- is produced in the *slow* reaction (1).

$$\begin{aligned}\text{Rate of production of } \text{I}_2 &= \text{Rate of production of } \text{IO}^- \\ &= k \cdot [\text{I}^-][\text{H}_2\text{O}_2].\end{aligned}$$

Thus the reaction between iodide and hydrogen peroxide in acid solution is not an example of the failure of the law of mass action, *when the law is correctly applied*.

Binary collisions, between pairs of molecules, last only a very short time, measured by a second divided by many powers of ten, and a triple collision involving three molecules must be accomplished in this short interval. Triple collisions are therefore very much rarer than binary. For example, it may be shown by applying the detailed kinetic theory that in gaseous oxygen

$$\frac{\text{Triple collisions } (3\text{O}_2)}{\text{Binary collisions } (2\text{O}_2)} = 10^{-3}.$$

Moreover, in a triple collision the preferred orientation I^- , H_2O_2 , I^- , due to repulsion of ionic charges, would be unfavourable to the formation of iodine molecules, by reactions such as $2\text{I}^- + \text{H}_2\text{O}_2 = 2\text{OH}^- + \text{I}_2$ and $2\text{OH}^- + 2\text{H}^+ = 2\text{H}_2\text{O}$. We see therefore that it is very improbable that a measurable rate of reaction can follow from triple collisions. Chemical reactions must proceed in *bimolecular* stages, i.e. in stages involving only binary collisions; and it is only for those very simple reactions which are completed in one such stage that a true expression for the rate of reaction can be deduced immediately from the equation of the reaction.

Chemical Equilibrium. We saw in Chapter XI that a state of equilibrium is reached when the free energy of a chemical system is at its minimum, and that reaction can be initiated from either side of the chemical equation representing the equilibrium, to reach ultimately the same point of equilibrium (see Example (1), p. 134); further, that the equilibrium quotient and the equilibrium constant characteristic of the equilibrium can be correctly deduced from that equation, *however complicated it may be*. Information about the mode of chemical reaction, and in particular of the distinct and numerous stages we have now seen may be involved, is irrelevant to the application of *the law of mobile equilibrium*, in extreme

contrast to the application of *the law of mass action*, wherein, on the contrary, the overall equation may be irrelevant.

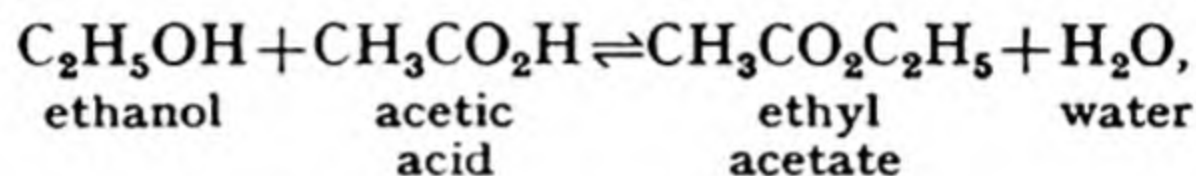
From the point of view of rates of reaction a chemical equilibrium must be a *dynamic* state, involving equality of rates of reaction in opposed directions. For the equilibrium $A + B \rightleftharpoons C + D$:

$$\text{Rate}_{A,B} = k_1[A][B] = \text{Rate}_{C,D} = k_2[C][D],$$

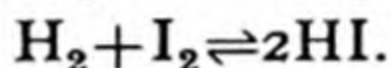
when the concentrations are those at equilibrium.

$$\therefore \frac{[C][D]}{[A][B]} = \frac{k_1}{k_2} = K, \text{ the equilibrium constant.}$$

Such a relation between velocity constants and equilibrium constant was proved experimentally by BERTHELOT and SAINT-GILLES for the equilibrium:



and by BODENSTEIN for the gaseous equilibrium:



In each of these equilibria the reaction on each side is completed in one bimolecular stage, and, as we have seen in the preceding section, it is only to such reactions that the law of mass action can be applied directly, as above. Hence *it is impossible to base a general law of equilibrium on the law of mass action.*

CHAPTER XV

CATALYSIS

This sad catalysis and declension of piety.

JOHN EVELYN.

IN 1835, BERZELIUS applied the term *catalytic agent*—now usually abbreviated to *catalyst*—to describe those substances which alter the rate of chemical reactions without themselves undergoing any permanent change in weight or in chemical composition. Among the examples of catalysis known to Berzelius were the decomposition of hydrogen peroxide by metals (THENARD, 1818), the hydrolysis of starch to dextrins and sugars by boiling with dilute acids (KIRCHOFF, 1811), and the ignition of combustible gas mixtures by means of platinum wire (EDMUND DAVY, 1817) or platinum sponge (DÖBEREINER, 1823). More generally familiar is the catalytic effect of manganese dioxide upon the decomposition of potassium chlorate by heat; but in point of fact catalysis is one of the commonest as well as one of the most valuable of chemical phenomena.

The principal features of catalytic change—most of which were indicated by OSTWALD in 1888—are as follows:

1. *A catalyst remains unchanged in weight and in chemical composition at the end of the reaction.* It may, however, be changed in physical respects. If, for instance, granular manganese dioxide is heated with potassium chlorate, it remains after the action as a powder. Smooth platinum, again, after use as a catalyst, is frequently found to have become roughened and pitted.

2. *A catalyst does not alter the products of the reaction in which it is used.* Potassium chlorate, for example, when heated alone finally yields potassium chloride and oxygen; if manganese dioxide is added as a catalyst, the products are still potassium chloride and oxygen. Similarly, when methyl acetate, $\text{CH}_3\text{COOCH}_3$, is heated with water, acetic acid, CH_3COOH , and methyl alcohol, CH_3OH , are formed. If a mineral acid is added, to act as a catalyst, the products are unchanged.

On the other hand, if several reactions are proceeding simultaneously, different catalysts may accelerate the individual reactions

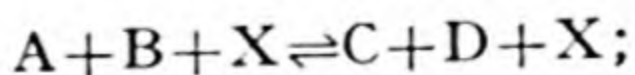
differently. Thus between carbon monoxide and hydrogen the following reactions may occur:

- (i) $\text{CO} + 3\text{H}_2 = \text{CH}_4$ (methane) + H_2O .
- (ii) $\text{CO} + \text{H}_2 = \text{H}.\text{CHO}$ (formaldehyde).
- (iii) $\text{CO} + 2\text{H}_2 = \text{CH}_3.\text{OH}$ (methyl alcohol).

Reaction (i) is catalysed more than the others by metallic nickel; reaction (ii) by metallic copper; and reaction (iii) by a mixture of zinc oxide and chromium sesquioxide, Cr_2O_3 .

3. *A catalyst alters the rate of the reaction in which it is employed.* This point may be well illustrated by heating potassium chlorate to such a temperature that the molten salt is just beginning to evolve oxygen; if now a pinch of manganese dioxide is introduced, the mass froths up owing to the abundant liberation of oxygen.

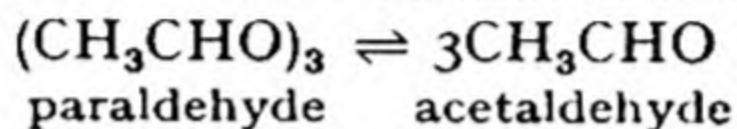
4. *A catalyst causes no change in the normal state of a chemical equilibrium.* In other words, the rates of the two opposing reactions of the system are affected to the same degree by the introduction of a catalyst. That this behaviour is a necessary consequence of the law of the conservation of energy was shown by VAN'T HOFF, using the following argument. Suppose, in the reversible reaction $\text{X} \rightleftharpoons \text{Y}$, that the forward action, $\text{X} \rightarrow \text{Y}$, is accompanied by the evolution of heat; then the opposing reaction, $\text{Y} \rightarrow \text{X}$, will be accompanied by an equivalent absorption of heat. Suppose further that a given catalyst accelerates the action $\text{X} \rightarrow \text{Y}$ more than it accelerates the action $\text{Y} \rightarrow \text{X}$. Then if such a catalyst were added to the system $\text{X} \rightleftharpoons \text{Y}$ in normal equilibrium the equilibrium would be displaced from left to right, and heat would be evolved, which could be used to drive a machine. If the catalyst were now withdrawn, the equilibrium would return to its original condition, the system absorbing the necessary heat from its surroundings. Re-introduction of the catalyst would cause a second displacement of the equilibrium, with liberation of a second amount of heat, and by repetition of the process an inexhaustible supply of heat would be attainable and the machine might therefore be kept in perpetual motion. Such a result is inconsistent with the conservation of energy and in particular with the second law of thermodynamics; hence the state of equilibrium must be independent of the presence or absence of a catalyst. A simpler but more general proof, since it does not depend on whether a reaction releases or absorbs heat, derives directly from (1) above. Whatever its mode of action may be, a catalyst has the unique property of appearing both as reactant and product:



its entries in the equilibrium quotient must therefore cancel out.

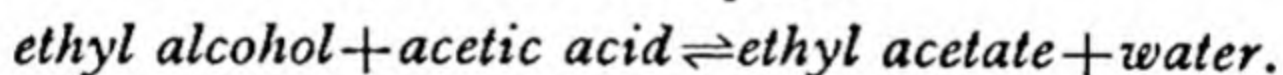
Experimental proof of the principle just described was provided by HAUTEFEUILLE and LEMOINE, who obtained the figures 0.19 and 0.186 respectively for the degree of dissociation of hydrogen iodide (a) in the presence of a catalyst and (b) in the absence of a catalyst, at 350°.

A corollary of the above argument is that the position of equilibrium should be independent of the nature of the catalyst; and this was proved by TURBABA, who showed that in the system



sulphur dioxide, zinc sulphate, oxalic acid, and other catalysts gave equilibrium positions approximating very closely to one another.

If the quantity of catalyst employed is great enough to be comparable with the quantities of the reacting substances, the conditions are so different that a displacement of the equilibrium may then occur. This is exemplified by the work of JONES and LAPWORTH on the equilibrium constant in the system:



The normal value of K in the equation

$$K = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5] \cdot [\text{H}_2\text{O}]}{[\text{C}_2\text{H}_5\text{OH}] \cdot [\text{CH}_3\text{COOH}]}$$

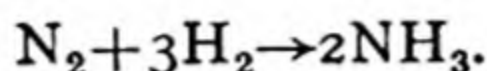
is approximately 4; but Jones and Lapworth found that in the presence of large quantities of hydrochloric acid, as catalyst, the value of K was more than doubled, rising to 8.83 when the ratio of HCl to water was 0.217. The effect may be attributed to the alteration of the effective concentration of water by the presence of much (ionized) hydrochloric acid.

5. *A catalyst cannot start a reaction which does not proceed without it, but merely accelerates a reaction already proceeding.* This postulate turns upon the fact that reactions proceeding at a lively rate on the molecular (not gram-molecular) scale may still be far beyond the bounds of practical detection. Suppose, for example, that in the absence of a catalyst such as finely divided platinum (see above) hydrogen and oxygen steadily combined to give 1,000 molecules of water per second. Then since 18 gm. of water contain 6.0×10^{23} molecules, 10^7 years must elapse before one millionth of a gram of water has accumulated.

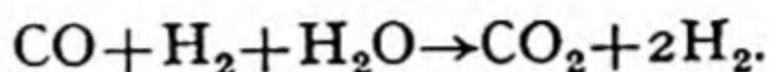
Types of Catalysis. There are two main types of catalysis, viz. *homogeneous catalysis* and *heterogeneous catalysis*. In homogeneous catalysis, both catalyst and reactants are in the same phase, while in heterogeneous catalysis the catalyst forms a phase in contact with the reactants at a definite boundary: hence the term *contact* (or *surface*) *catalysis*.

Heterogeneous Catalysis. Among the more important examples of heterogeneous catalysis are:

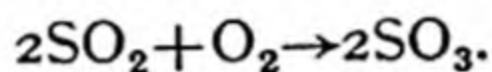
1. The direct combination of nitrogen and hydrogen to form ammonia, as in the HABER process (see p. 430). Here the catalyst is iron formed by reducing iron oxide *in situ*.



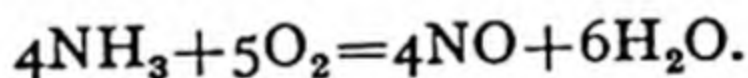
2. The formation of hydrogen and carbon dioxide from water-gas and steam (p. 275). The catalyst consists mainly of iron.



3. The formation of sulphur trioxide from sulphur dioxide and atmospheric oxygen (p. 530). Platinum, and vanadium pentoxide or silicate, are the catalysts most frequently used.

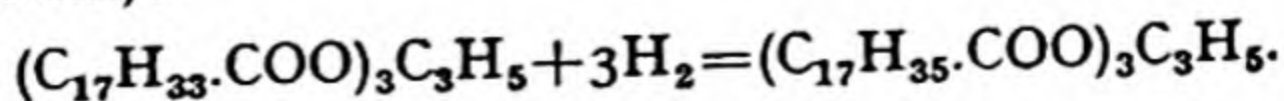


4. The oxidation of ammonia to nitric oxide, as in the synthetic process for the manufacture of nitric acid (p. 447). The action is catalysed very smoothly by platinum and by various metallic oxides, e.g. a mixture of ferric oxide and bismuth oxide, or of ferric oxide and lanthanum oxide.



5. The synthesis of methyl alcohol from water-gas and hydrogen. The catalyst may be a mixture of zinc oxide and chromium oxide, though other substances have been recommended. A remarkable fact is that iron inhibits the formation of methyl alcohol, and care has to be taken to remove even traces of this metal from the plant and from the reacting gases.

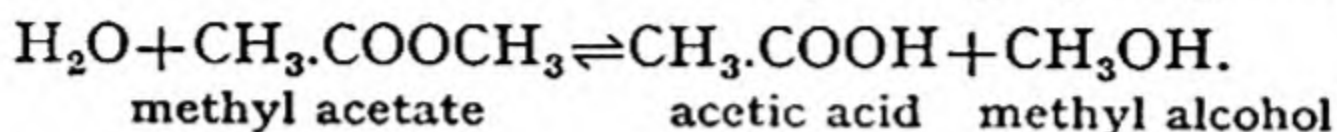
6. The 'hardening' or hydrogenation of oils. This consists in the reduction, by gaseous hydrogen, of the glyceryl esters of certain unsaturated acids; the products are the glyceryl esters of the corresponding saturated fatty acids. They have higher melting-points than the unsaturated esters, which are usually oils while the hydrogenated esters are semi-solid at ordinary temperatures, and are known as fats. The hydrogenation of oils has great commercial importance, since the fats so produced are used as the basis of artificial lard, etc., and for the manufacture of soap. The catalyst employed is nickel, normally at a temperature of 100° to 180° , and the reaction may be exemplified by the following equation, which shows the reduction of glyceryl oleate (an oil) to glyceryl stearate (a fat):



Homogeneous Catalysis. Here the catalyst is in the same phase (p. 163) as the reactants.

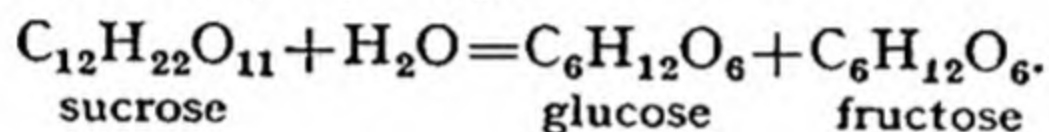
Examples: (i) Oxides of nitrogen act as a catalyst in the chamber-process for the manufacture of sulphuric acid (p. 531).

(ii) The hydrolysis of esters is catalysed by hydrogen ions, e.g.:



Methyl acetate is slowly hydrolysed by pure water, but the addition of a little acid greatly increases the speed at which equilibrium is reached. This reaction is used as a means of comparing the strengths of acids, i.e. their relative degree of dissociation at equivalent concentrations, since the magnitude of the catalytic effect is proportional to the concentration of hydrogen ions.

(iii) The inversion of sucrose (cane-sugar), i.e. its conversion into a mixture of the two isomeric sugars glucose and fructose, is also catalysed by hydrogen ions:



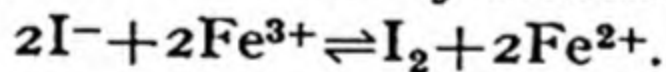
The mixture of glucose and fructose is called invert-sugar. Sucrose and invert-sugar have different effects upon plane-polarized light; hence the course of this reaction may be followed if the solution is examined in a polarimeter.

Like the hydrolysis of esters, the inversion of sugar has been employed as a means of comparing the strengths of acids.

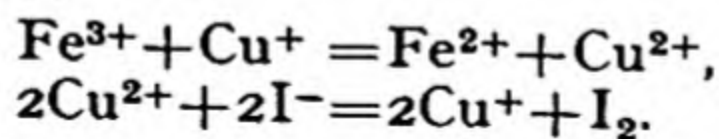
Theories of Catalytic Action.

Homogeneous Catalysis.

There is no doubt that a homogeneous catalyst is to be regarded as a reactant, and the reaction as proceeding in stages, in the last of which the catalyst reappears. The oxidation in dilute solution of iodide ion I^- by ferric ion Fe^{3+} slowly reaches an equilibrium:

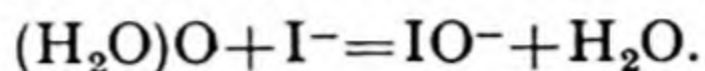


The rate at which the equilibrium is approached is enormously increased by the presence of even a trace of cuprous ion, Cu^+ , which participates as follows:

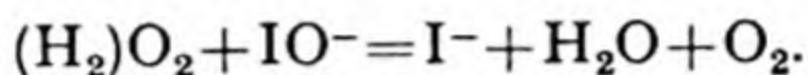


Both ionic reactions are known to be very fast, and the reappearance of cuprous ion in the second gives this ion its catalytic status.

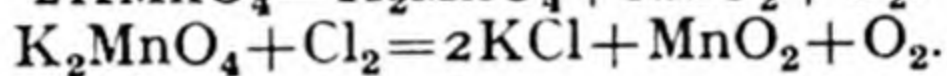
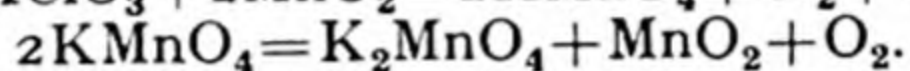
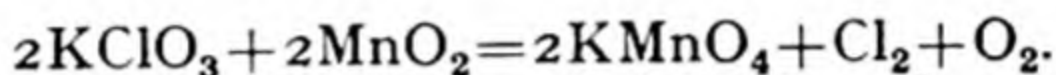
The decomposition of hydrogen peroxide into water and gaseous oxygen is greatly accelerated by iodide ion. In the first stage of the decomposition the peroxide acts as oxidized water $(\text{H}_2\text{O})\text{O}$:



In the absence of acid (to produce hypoiodous acid, HIO) the anions I^- and IO^- do not interact, but a second molecule of peroxide, acting now as reduced oxygen $(\text{H}_2)\text{O}_2$, converts the latter back into iodide:

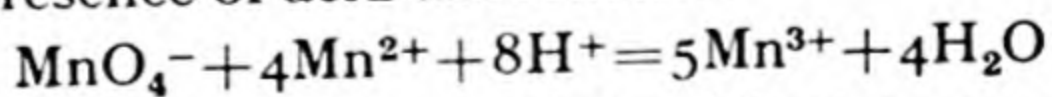


It has been suggested that the effect of manganese dioxide upon the decomposition of potassium chlorate is explained by the series of reactions:



Beyond the fact that potassium permanganate decomposes at a much lower temperature than potassium chlorate it cannot be said that much experimental evidence supports this scheme, which is, however, plausible. It is based upon an alternation of the valency of manganese between IV in the dioxide and VII in permanganate: it is hence interesting that both cobaltous oxide, CoO , and nickelous oxide, NiO , also exert catalytic influence: each of these oxides can pass into a less stable sesquioxide, Co_2O_3 and Ni_2O_3 , with the valency change II-III.

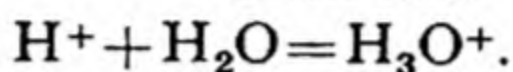
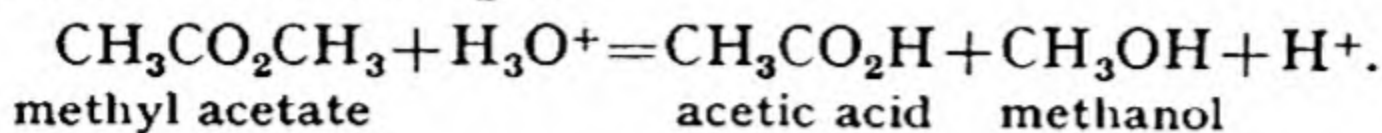
A catalytic agent may appear as one of the normal products of a reaction—its activity is then termed *auto-catalysis*. If to a solution of oxalic acid at room temperature a few drops of a solution of potassium permanganate are added, the pink coloration remains undischarged, but disappears instantly upon adding a drop of a solution of manganous sulphate. From this point permanganate solution may be rapidly added in bulk and the equally rapid oxidation of the oxalic acid is signaled by the effervescence of carbon dioxide. It is very probable that permanganate *per se* is not a powerful oxidizing agent, but when manganous ion Mn^{2+} is added in the presence of acid the reaction



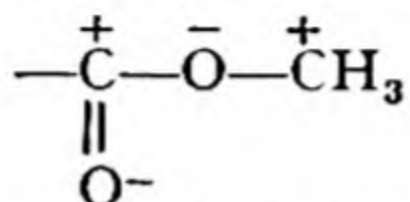
takes place, producing the powerful oxidant manganic ion, Mn^{3+} . Once reaction has started the supply of manganous ion of course increases *pari passu* with the decomposition of permanganate.

The hydrogen ion, H_3O^+ in aqueous solution, exhibits a very widespread catalytic activity, particularly in reactions of *hydrolysis*,

i.e. decompositions by reaction with water. Such hydrolytic changes occur in two stages:



In the ester the carbon-oxygen links are highly *polar* (p. 111):

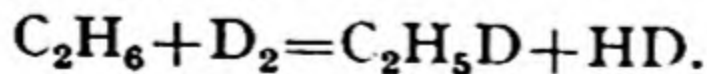


and either of the ions H_3O^+ or OH^- can be drawn by electrical forces into the ester structure to points strategically well placed for the chemical actions, of *saponification* by hydroxyl ion (which is not reproduced in the action) or of catalytic hydrolysis by H_3O^+ .

Heterogeneous Catalysis.

If we consider the surfaces formed by fracturing a piece of metal or of some ionic compound we see that many of the atoms or ions lying in the surfaces must be in a chemically 'unsaturated' state. Gases in contact with the surface therefore condense upon it under the agency of strong chemical forces: such condensation is termed *chemisorption*. The role of the surface as a catalyst lies in the possibility that the chemical energy of its atoms may be at least partially transferred to the condensed gas, which may in that way receive a notable contribution to the activation energy it needs for its own chemical actions (p. 179).

The well-known effect of a platinum surface in causing the equilibrium $2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2$ to be rapidly reached is probably due to the formation on the catalyst surface of a conjunction of activated molecules similar to that indicated in the diagram discussed on p. 178. Two molecules of HI, after condensing on neighbouring sites, may evaporate from the surface as H_2 and I_2 , and conversely. Much insight has recently been gained into the mechanism of surface catalysis by studying examples of '*exchange reactions*.' This is the term used to describe the substitution in a compound of one isotope for another of the same element, e.g. deuterium for hydrogen. When a mixture of ethane, C_2H_6 , and deuterium is exposed at moderate temperatures to the surfaces of metals, e.g. nickel, copper, or palladium, which are efficient catalysts in hydrogenation reactions (p. 186), deuterium is exchanged for hydrogen in successive reactions, of which the first is:



It is found that the experimental facts may be adequately explained by supposing that the metal surface covers itself with a

layer of activated molecules of deuterium. The advantage of studying such exchange reactions is that the stabilities of hydrides and deuterides are precisely equal, and hence attention may be focused exclusively on the surface conditions.

'Poisoning' of Surface Catalysts. Competition for its available surface will arise when mixtures of gases are in contact with a solid. If a particular gas is very strongly attached it may, even when present at a small partial pressure, exclude a second gas less responsive to the surface attraction. In the application of 'contact' processes in industry great care is necessary to free reacting gases from traces of 'poisons,' that is, volatile impurities that are very strongly chemisorbed on the catalysts, such as arsenic compounds in the manufacture of sulphuric acid (p. 530). The modern substitution of vanadium pentoxide for platinum in the sulphuric acid process is largely due to its greater resistance to 'poisoning.' It is probable that the pentoxide operates through alternate reduction by chemisorbed sulphur dioxide and reoxidation by the oxygen in the gas mixture.

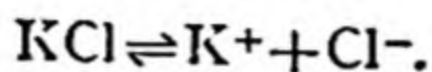
Inhibiting Agents. It is not infrequently necessary to prevent or at least decelerate a chemical action. Many synthetic rubbers lose their desirable properties as they become slowly oxidized in the atmosphere. Various phenolic compounds when added to the rubber 'mix' inhibit or greatly diminish the rate of this deleterious oxidation. The combination with oxygen is *autocatalytic*, i.e. it produces its own catalyst, and the inhibitors operate by side-tracking the catalyst, that is, by forming stable compounds with it.

CHAPTER XVI

ELECTROLYTIC DISSOCIATION

Theories of Electrolysis. The earliest theory of electrolysis was put forward in 1805 by GROTHUS, only three years after the first electrolysis of water by NICHOLSON and CARLISLE. The details of the theory, which included the execution of a kind of Paul Jones dance by neighbouring molecules of the electrolyte, are of merely antiquarian interest; the important point to note is that GROTHUS made the very natural assumption that the breaking up of the electrolyte molecules was actually *caused by the current*. If this were so, it is clear that electrical energy would be consumed in the process; but measurement shows that, in point of fact, a solution of an electrolyte obeys OHM's Law—in other words, the whole of the electrical energy is employed in overcoming the resistance of the solution, and no part of it is used for the disruption of electrolyte molecules. A choice of alternatives is left: either the disruption of the electrolyte can take place without the use of energy, or the electrolyte is broken up into its charged particles even before the current passes. Of these two alternatives, the former seems obviously absurd, while the second appeared almost equally absurd in the early years of the nineteenth century.

In 1857, however, CLAUSIUS suggested that a small fraction of the molecules of a dissolved electrolyte might spontaneously dissociate into ions. On passage of the current, these would be discharged, and successively replaced by the spontaneous disruption of further molecules; so that in the end the whole of the electrolyte might be broken up. Thirty years later (1887) ARRHENIUS was bold enough to advance the hypothesis that, instead of a small fraction, a large fraction of an electrolyte underwent this spontaneous *ionization* in solution, and that at great dilution the ionization might be complete. To take a particular example we may select potassium chloride. According to Arrhenius, a moderately dilute solution of this substance will contain a certain number of un-ionized KCl molecules, together with a large proportion of potassium ions, K^+ , and chlorine ions, Cl^- . The number of potassium ions is of course equal to that of chlorine ions, and the ions were considered to be in equilibrium with the un-ionized molecules:



The equilibrium is dynamic, i.e. ions are recombining to form un-ionized molecules at the same rate as un-ionized molecules are splitting up into ions.

On dilution of the solution, the equilibrium is moved in the direction of greater ionization, until at infinite dilution the whole of the potassium chloride exists as potassium ions and chlorine ions.

Arrhenius's theory did not at first receive general acceptance,



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FIG. 43. SVANTE ARRHENIUS

mainly because chemists failed to realize that an electrically charged atom or radical might possess chemical properties very different from those of the same atom or radical in the unelectrified state. They felt that since potassium attacks water with violence, it was incredible that a solution of potassium chloride contained a large number of free potassium atoms, even admitting that those atoms were highly charged. In the course of time, however, evidence in favour of the ionic hypothesis became so strong that this objection was waived; and modern knowledge of atomic structure has shown that, in direct opposition to the older view, the chemical properties of atoms are in fact intimately and fundamentally connected with their electrical condition.

Another difficulty experienced by Arrhenius's theory was based upon considerations of energy changes. Still using potassium chloride as an example, we may recollect that potassium and chlorine unite with the evolution of large quantities of energy. If potassium chloride, on mere solution in water, decomposes in great part into potassium and chlorine atoms, whence comes the energy apparently necessary for this decomposition? Here again, the criticism rests partly upon a misconception; for it is into potassium and chlorine *ions*, not into potassium and chlorine *atoms*, that the potassium chloride splits up. It does not at all follow that the *ionization* of potassium chloride would require the supply of as much energy as its decomposition into metallic potassium and gaseous chlorine. Supposing the energy needed for ionization to be small, it might possibly be derived from the energy of the solvent molecules; so that the difficulty did not appear to be insuperable. Meanwhile, the success of Arrhenius's theory in explaining and correcting the most varied types of chemical phenomena was so striking that, whatever criticisms were levelled against it, little doubt remained that it possessed a large element of truth.

To-day the essential distinction between 'strong' and 'weak' electrolytes (p. 35) has become clear as a structural difference. Crystals of the former class, which includes nearly all known salts, are constituted solely of ions, in regular arrangement, and dissolution in water merely serves to disperse these ions. 'Weak' electrolytes, such as acetic acid and many other acids, are, on the contrary, composed of molecules, which undergo electrolytic dissociation by dissolution in water. For the latter class, as we shall see, the views of Arrhenius remain entirely acceptable.

The Equivalent Conductance of Electrolyte Solutions. The *equivalent* of an ion depends on (1) whether, as below, we consider it as transporting electrical charge in discussing the conductance of electrolyte solutions, or (2) whether we have in mind the chemical reactions in which the ion can take part. Under the head (1) *the equivalent of an ion is that weight which bears a charge (+ or -) of one faraday*. Thus the equivalent in grams is the gram-ionic weight divided by the charge in faradays. For ions with one charge (H^+ , Na^+ , Cl^- , OH^-) the equivalent is the same as the gram-ionic weight: for those with two charges (Ba^{2+} , Cu^{2+} , SO_4^{2-}) or three charges (Al^{3+} , Fe^{3+} , PO_4^{3-}) it is one-half or one-third of the gram-ionic weight respectively. The corresponding equivalent of a *salt* is that weight of it which contains the equivalents of the ions composing it; e.g. for $BaCl_2$ the equivalent is $\frac{G.F.W.}{2}$.

Under the head (2) the ionic equivalent is not invariable as under (1) but depends on the chemical reaction concerned. The most

important of the reactions in which ions take part are those of oxidation and reduction discussed in Chapter XVIII.

The *specific conductance* κ of a conductor, metallic or electrolytic, is, by Ohm's Law, numerically equal to the current in amperes (coulombs/sec.) flowing between two opposite faces of a cube of the conductor of 1 cm. side, when an electromotive force of 1 volt is applied between those faces. The *specific resistance* is the reciprocal of the specific conductance. To form a correct conception of an electrolytic conductor it is to be remembered that in a solution at ordinary temperature the ions, in common with the molecules of solvent, are in vigorous thermal motion in random directions. The effect of the imposed electric field (1 volt/cm.) is to remove *to a very small extent* the randomness of this motion. We shall see later that the consequent drift speed of ions through the solution is very much less than the average thermal speed. In the following pages the term *speed of an ion* (symbol u_+ or u_-) will imply only the drift speed.

As an example of an electrolytic conductor consider a solution of barium chloride, BaCl_2 , containing 1 gm.-equivalent, or 104.1 gm., of the salt per litre. Such a solution must contain $\frac{1}{2}$ gm.-ion of Ba^{2+} (charge $2F$ coulombs) and 1 gm.-ion of Cl^- (charge $-F$ coulombs) per litre; in 1 c.c. of solution there is $\frac{0.001}{2}$ and 0.001 gm.-ion respectively. If the speeds of the ions in the field of 1 volt per cm. are u_+ and u_- cm. per second, then the electric current i equal to the specific conductance is

$$i = \kappa = \frac{0.001}{2} \cdot 2Fu_+ + \frac{0.001}{1} \cdot Fu_- \\ = c(Fu_+ + Fu_-),$$

where c is the concentration of the electrolyte in gm.-equivalent per c.c. (see p. 193). The products Fu_+ and Fu_- (one faraday \times ionic speed) are termed the *mobilities* of the ions and are usually given the single symbols λ_+ and λ_- . The volume $v = \frac{1}{c}$ is the volume in c.c. of the solution containing 1 gm.-equivalent of the salt. The quantity κv is termed the *equivalent conductance* of the solution. In words:

Equivalent conductance = specific conductance \times volume in c.c. containing one gm.-equivalent of electrolyte.

Since $\kappa v = \lambda_+ + \lambda_-$ we can also state:

Equivalent conductance = sum of the mobilities of the ions composing the electrolyte.

The *dilution* V of an electrolyte solution is defined as the volume in litres containing 1 gm.-equivalent of electrolyte. This quantity is expressed in litres to avoid the inconveniently large numbers required to express it in cubic centimetres for dilute solutions of electrolyte. Hence in calculations of equivalent conductance from given data of specific conductance and dilution the relation to be used is:

Equivalent conductance = specific conductance \times dilution $\times 1,000$.

Electrical conductance is expressed in terms of the unit ohm⁻¹ or *mho*, since the ohm, in which its reciprocal, resistance, is expressed, is a fundamental electrical unit. The unit of equivalent conductance is mho/gm.-equivalent.

Application of the Equivalent Conductance. The usefulness of the equivalent conductance as an experimental quantity may be seen from the following considerations:

(i) Suppose that in an electrolyte solution at different dilutions V , the total number n of gm.-ions, and the ionic mobilities λ_+ and λ_- remain constant. Then the specific conductance κ would decrease in proportion to the concentration $\frac{n}{V}$:

$$\kappa = \text{a constant} \left(\frac{n}{V} \right), \text{ and } 1,000\kappa V = \text{a constant.}$$

Thus if a series of measurements of specific conductance at different dilutions should ever give the result that the equivalent conductance is constant we could be confident that both the number of ions and their mobilities were constant.

(ii) Now suppose, with Arrhenius, that the total number of ions is not constant but increases with dilution, for example by chemical dissociation of electrolyte molecules (p. 191), but their mobilities do not change. Then again $\kappa = \text{a constant} \left(\frac{n}{V} \right)$, and $1,000\kappa V = \text{a constant} \times n$. In this case the equivalent conductance increases in direct proportion to the number n of ions.

(iii) Conversely, if the number of ions was constant but their mobilities changed with dilution, then since equivalent conductance is the sum of the mobilities it is a direct measure of the change of mobility.

We see that the equivalent conductance can give a clear insight into the behaviour of the electrolyte in different ways. It should be understood that in *all* the cases considered above the *specific* conductance *decreases* with increased dilution.

Equivalent Conductance and Dilution. The relation between equivalent conductance and the dilution V typical of salt solutions is depicted in curve A, Fig. 44. Putting $\lambda_+ + \lambda_-$ equal to Λ_V we see that Λ_V increases rapidly to a maximum Λ_∞ beyond which it does not measurably change, however great the dilution. Hence Λ_∞ is often called the equivalent conductance 'at infinite dilution.' The ratio $\Lambda_V/\Lambda_\infty = \beta$ is known as the *conductance ratio*. For solutions of

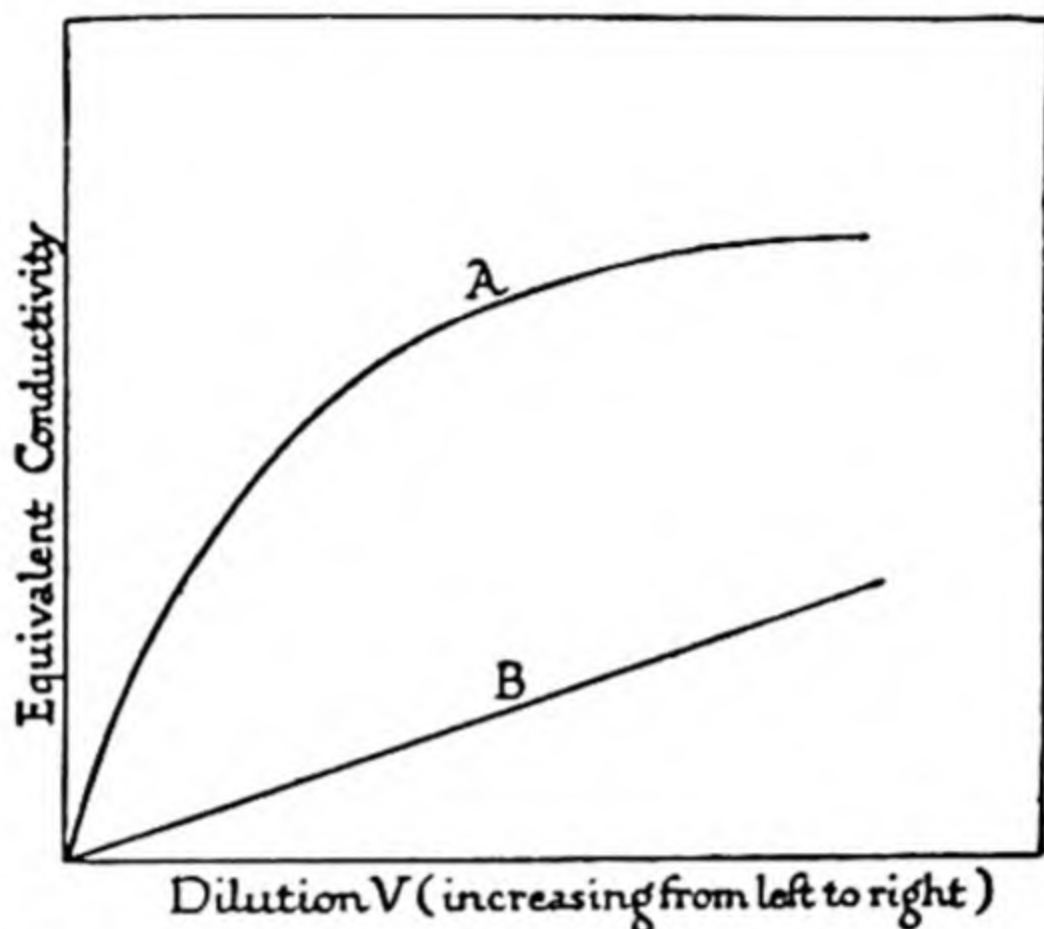


FIG. 44. EFFECT OF DILUTION ON EQUIVALENT CONDUCTANCE (CONDUCTIVITY) *

salts with equally charged ions, such as NaCl or MgSO_4 , KOHL-RAUSCH (1840-1910) showed experimentally that the ratio β is related to equivalent concentration c according to the equation:

$$\beta = 1 - A\sqrt{c},$$

the constant A being specific for each electrolyte. This means that a plot of β against \sqrt{c} yields a linear graph, cutting the β axis ($c=0$) at the value unity.

Ionic Mobility and Dilution. Since at all dilutions the number n of ions in a salt solution must remain the same, we are presented in curve A, Fig. 44, with an example of case (iii), p. 195, and we conclude that as the average distance between ions becomes greater, ionic mobility undergoes a steady and rapid increase until it reaches an apparent maximum, corresponding to Λ_∞ , the equivalent conductance 'at infinite dilution.'

Any solution of an electrolyte is *electroneutral*, i.e. the charges on the cations are exactly balanced by those on the anions. Such

* The term *conductance* is now preferred to *conductivity*.

general electroneutrality is however compatible with *local* variation from strict balancing. Owing to attraction between ions of unlike charge and repulsion between those of like charge the anions in the neighbourhood of any cation are slightly nearer to it than the surrounding cations, and conversely for any anion. In this way any ion in solution becomes surrounded by a slight excess of opposite charge, which, while negligible at 'infinite' dilution, steadily increases in magnitude with increase of total ionic concentration. We might say that vestiges of the crystal structure survive in solution to a greater extent the greater the ionic concentration. In an electric field the charged 'atmospheres' tend to move in the opposite direction to that of the central ion, upon the motion of which a 'drag' is thus imposed. In short the speeds u_+ and u_- , and hence the mobilities λ_+ and λ_- , decrease steadily with increase of ionic concentration. In 1923 DEBYE and HUCKEL published calculations of this effect, and showed that it accounted *completely* (in dilute solution) for the change of conductance ratio β with change of concentration c , according to Kohlrausch's relation given many years before (p. 196). Since the effect described must operate in all solutions containing ions the increase in the actual number of ions postulated by Arrhenius to explain the rise of equivalent conductance with increasing dilution is excluded. As is to be expected, and as the table shows, the conductance ratio for a given concentration of salt is smaller the higher the charges on the ions:

Equiv./litre	Conductance Ratio (β)			
	0.01	0.05	0.20	0.50
KCl	0.943	0.885	0.833	0.800
K ₂ SO ₄	0.872	0.771	0.673	0.618
BaCl ₂	0.883	0.798	0.720	0.672
K ₄ Fe(CN) ₆	—	0.634	0.520	0.425

Ionic Mobility at 'Infinite Dilution.' At high dilution the electrical interaction of ions explained in the preceding paragraph must become negligible, and equivalent conductance, which is the sum of the ionic mobilities λ_+ and λ_- , reaches its maximum. Hence both λ_+ and λ_- must separately attain their maxima, and become *independent* and *characteristic* properties of the ions concerned. That this is true was demonstrated as early as 1875 by Kohlrausch, who anticipated the later views of Arrhenius (1887) in his *law of the independent migration of ions*. This law states that the equivalent conductance of an electrolyte solution at infinite dilution, Λ_∞ , may be expressed as the sum of two parts, one specific to the cation, $\infty\lambda_+$, and the other to the anion, $\infty\lambda_-$.

Kohlrausch found, for example, that the values of Λ_{∞} for potassium chloride, sodium chloride, potassium nitrate, and sodium nitrate were as follows:

KCl	130.10	KNO ₃	126.50
NaCl	108.99	NaNO ₃	105.33
Difference	<u>21.11</u>	Difference	<u>21.17</u>
KCl	130.10	NaCl	108.99
KNO ₃	126.50	NaNO ₃	105.33
Difference	<u>3.60</u>	Difference	<u>3.66</u>

That is, the difference between Λ_{∞} for the chloride and the nitrate of a metal is the same whether the metal is sodium or potassium; and the difference between Λ_{∞} for potassium and sodium salts is independent of the nature of the anion.

The Freezing-points and Osmotic Pressures of Ionic Solutions. The Dutch chemist, VAN'T HOFF, a contemporary of Arrhenius, in an exhaustive study of osmotic pressures and the depression of freezing-point of aqueous solutions of salts, laid the foundations of our accurate knowledge of this subject. He expressed his observations by using a coefficient $i = \frac{(\text{experimental effect})}{(\text{calculated effect})}$, where the denominator is the effect (osmotic pressure or depression of freezing-point) to be expected if a salt acted as a single molecular species with molecular weight identical with its gram-formula weight, and the numerator is the effect observed. Later workers have also availed themselves of this mode of expression.

It will be seen from the table that at the lowest concentrations, where any kind of ionic interdependence must be very small, the values of i approach closely to n , the number of gm.-ions present in the gram-formula weight of the salts. This proves that the electric charge on an ion does not *inherently* prevent its playing the role of an uncharged 'particle' in the phenomena concerned. At higher concentrations i steadily decreases, and, as in the case of the conductivity ratio, at a greater rate the higher the ionic charges. Electrical interaction of ions thus appears again in osmotic phenomena. The *osmotic coefficient* g is defined as $\frac{i}{n}$, where n is, for example, 2 for NaCl or MgSO₄, 3 for K₂SO₄ or BaCl₂, 4 for AlCl₃ or K₃Fe(CN)₆, etc. The coefficients β and g are measures of the extent

to which the ions act independently in the two different phenomena of electrical conductivity and osmotic behaviour, the ideal condition postulated in each case being n completely independent ions.

van't Hoff's Coefficient, and Osmotic Coefficient

Conc. G.F.W./litre	0.0005	0.001	0.01	0.10	0.50
KCl ($n=2$)	—	1.99	1.94	1.86	1.80
	—	0.99	0.97	0.93	0.90
BaCl ₂ ($n=3$)	2.92	2.85	2.76	2.58	2.42
	0.97	0.95	0.92	0.86	0.81
K ₃ Fe(CN) ₆ ($n=4$)	3.95	3.84	3.43	3.01	2.71
	0.99	0.96	0.86	0.75	0.68

<i>Effect observed</i>	<i>Definition</i>	<i>Ideal</i>	<i>Actual</i>
Equivalent conductance	$1,000\kappa \cdot V_{\text{equiv.}}$	Λ_{∞}	$\beta \cdot \Lambda_{\infty}$
Molar freezing-point depression	$t^{\circ} \cdot V_{\text{G.F.W.}}$	$(n \times 1.860)^{\circ}$	$g(n \times 1.860)^{\circ}$
Osmotic pressure at 0° C. per G.F.W.	$P \cdot V_{\text{G.F.W.}}$	$(n \times 22.4) \text{ atm.}$	$g(n \times 22.4) \text{ atm.}$

$V_{\text{equiv.}}$, $V_{\text{G.F.W.}}$ = volume in *litres* containing 1 gm.-equivalent or 1 gm.-formula weight; κ = specific conductance; t° = observed depression of F.P.; P = observed osmotic pressure.

Both coefficients β and g tend to the value unity at 'infinite dilution,' and the expressions $1-\beta$ and $1-g$ measure the electrical interactions of the ions operating for electrical conductivity and osmotic phenomena respectively. For salts composed of ions of equal charges both follow the same type of relation for change of concentration:

$$1-y = (\text{a constant}) c^{\frac{1}{2}} \quad (y = \beta \text{ or } g),$$

but the constants are different for the two coefficients. This difference has the consequence, as the tables of β and g for some typical salts indicate, that for a given concentration of electrolyte these coefficients are not equal, g being the larger. There is no reason to suppose that the electrical interaction of ions would have an identical effect upon their mobilities and upon their power to decrease the vapour pressure of the solvent, which is the basic cause of depression of the freezing-point and of osmotic pressure (p. 154).

The Activity Coefficient of Electrolytes. We have seen earlier (Chapter XI) that the molar free energy of a dissolved substance may be expressed as

$$G = RT \log_e C + G_0,$$

where G_0 is the molar free energy at unit concentration, and C is the concentration. If the ions of an electrolyte such as potassium chloride acted quite independently of each other its free energy per G.F.W would be

$$G = 2RT \log_e C + G_0.$$

In conferring electrical conductivity on their solutions, and in their effect on the properties of the solvent shown in depression of freezing-point and in osmotic phenomena, ions are manifestly subject to mutual interaction, expressed quantitatively in the conductance ratio and the osmotic coefficient. It is therefore not surprising that their free energy should also be affected by such interaction, which is taken into account in the expression

$$G = 2RT \log_e f.C + G_0 = 2RT \log_e a + G_0.$$

Here a , called the *activity* of the electrolyte, is the *effective* concentration for computing the free energy. The activity is obtained by multiplying the concentration by the factor f , the *activity coefficient*. Like the other coefficients f is a fraction increasing to unity at 'infinite dilution.'

The free energy may also be expressed in terms of the free energies of the ions:

$$2RT \log_e f.C = RT \log_e f_+ C + RT \log_e f_- C.$$

From this we easily find $f^2 = f_+ f_-$. The coefficients f_+ and f_- are not necessarily equal, but as an ion cannot be studied in the absence of its oppositely charged counterpart there can be no means of determining these quantities separately. The *mean coefficient* $\sqrt{f_+ f_-} = f$ is therefore adopted for each ion. Whenever the free energy of ions is concerned, as in forming the equilibrium quotient of the law of mobile equilibrium for a system involving ions, it is the *activity*, $f.C = a$, which should be entered in place of concentration. It may be noted that the concept of activity is quite distinct from that of 'active mass' in Guldberg and Waage's law of mass action (Chapter XIV).

Activity Coefficients at 18°

Concentration (G.F.W./litre)	0.01	0.05	0.10	0.50	1.00
NaCl	0.903	0.821	0.778	0.678	0.658
HCl	0.904	0.830	0.796	0.757	0.809

Examples: (i) The equivalent conductance of hydrochloric acid at infinite dilution is 380 mhos. Find the equivalent conductance and the conductance ratio of N/50 hydrochloric acid given that its specific resistance is 137 ohms.

The specific conductance of N/50 HCl is

$$\frac{1}{137} = 0.0073 \text{ mhos.}$$

\therefore the equivalent conductance of N/50 HCl is
 $0.0073 \times 1000 \times 50,$

since 1 gm.-equivalent of HCl is contained in 50 litres of the N/50 acid.

\therefore conductance ratio

$$\begin{aligned} &= \frac{0.0073 \times 1,000 \times 50}{380} \\ &= \underline{0.96.} \end{aligned}$$

(ii) A solution of 35.5 gm. of anhydrous sodium sulphate in 1,000 gm. of water froze 1.00° below the freezing-point of water. Calculate the osmotic coefficient g of this solution and its osmotic pressure P at 0° . The freezing-point constant for water (100 gm.) is 18.6.

G.F.W. of Na_2SO_4 = 142.0 gm., $n = 3$ (gm.-ions).

$$\begin{aligned} \text{Ideal depression of F.P.} &= \left(3 \times \frac{35.5}{142} \times 1.860 \right)^\circ \\ &= 1.395^\circ. \end{aligned}$$

$$\text{Osmotic coefficient } g = \frac{1.00}{1.395} = 0.717.$$

For 1 G.M.W. per 1,000 gm. water at 0° osmotic pressure P
 $= 22.4 \text{ atm.}$

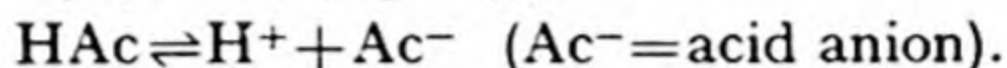
For the solution of sodium sulphate:

$$\begin{aligned} P &= 22.4 \times \frac{35.5}{142} \times 3 \times 0.717 \text{ atm.} \\ &= \underline{12.04 \text{ atm.}} \end{aligned}$$

Weak electrolytes. The course of the equivalent conductance of acetic acid with changing dilution is strongly contrasted with that of its salts, such as sodium acetate, in the typical curves B and A of Fig. 44. The conductance of the acid increases much less rapidly than that of the salt, and is still markedly rising at dilutions well beyond that at which the conductance of the salt has effectively

reached its maximum. For the acid Λ_{∞} cannot be directly observed since the *specific* conductance would have become far too small to measure accurately. The radical difference between the two curves must mean that the main reason for the rise of equivalent conductance is not increase of ionic mobility, since we see in curve A that this is far more sensitive to increasing dilution.

Let us provisionally assume, with Arrhenius, that a chemical equilibrium exists in solution between acid molecules and the ions produced by dissociation, and that increase of equivalent conductance is due to increase in the total number of these ions and not to change of mobility (case (ii), p. 195).



$$\frac{1-\alpha}{V} \quad \frac{\alpha}{V} \quad \frac{\alpha}{V}$$

Suppose that at the dilution V (litres) the concentrations are as shown above: we term α the *degree of (electrolytic) dissociation of the acid*. For $\alpha=1$, or total dissociation, the equivalent conductance is Λ_{∞} . Hence $\Lambda_v = \Lambda_{\infty} \alpha$ (see (ii), p. 195). If the assumptions are correct then the measured conductance ratio β is equal to the degree of dissociation α .

The value of Λ_{∞} for the weak electrolyte, which for the reason given above cannot be directly observed, is readily calculated by an application of Kohlrausch's law of independent migration—for acetic acid

$$\lambda_{\infty}(\text{K}^+) + \lambda_{\infty}(\text{Ac}^-) = \Lambda_{\infty}(\text{KAc}) = 99.6.$$

$$\lambda_{\infty}(\text{K}^+) + \lambda_{\infty}(\text{Cl}^-) = \Lambda_{\infty}(\text{KCl}) = 130.1.$$

$$\lambda_{\infty}(\text{H}^+) + \lambda_{\infty}(\text{Cl}^-) = \Lambda_{\infty}(\text{HCl}) = 379.4.$$

$$\text{Hence} \quad \lambda_{\infty}(\text{H}^+) + \lambda_{\infty}(\text{Ac}^-) = 99.6 + 379.4 - 130.1 = 348.9,$$

and for acetic acid

$$\alpha = \frac{\Lambda_v}{\Lambda_{\infty}} = \frac{\Lambda_v}{348.9}.$$

Ostwald's Dilution Law for Weak Electrolytes. The German chemist OSTWALD (1853–1932) perceived that if the equilibrium suggested above exists, then it must be subject to the law of mobile equilibrium (p. 127):

$$\frac{[\text{H}^+][\text{Ac}^-]}{[\text{HAc}]} = K_a,$$

where K_a is the *electrolytic dissociation constant* for the acid.

Therefore

$$\frac{\frac{\alpha}{V} \cdot \frac{\alpha}{V}}{\frac{1-\alpha}{V}} = \frac{\alpha^2}{(1-\alpha)V} = K_a.$$

Ostwald himself carried out numerous measurements to discover how far this *dilution law* is obeyed. His results for acetic acid are typical:

Ionization of Acetic Acid in Aqueous Solution at 25° C.		
V	$\alpha \left(= \frac{\Lambda_v}{\Lambda_\infty} \right)$	$K \left(= \frac{a^2}{(1-a)V} \right)$
5.374	0.0098	18.1×10^{-6}
10.573	0.0138	18.0×10^{-6}
24.875	0.0216	19.2×10^{-6}
63.26	0.0336	18.5×10^{-6}

The constancy of K_a is fully confirmed, and the existence of the dissociation equilibrium thereby proved. Since α is small compared with unity for moderate dilutions we may calculate $\frac{\alpha}{V}$, the concentration of the ions, by the good approximation:

$$\frac{\alpha^2}{V} = K_a$$

$$\text{or } \frac{\alpha}{V} = \sqrt{\frac{K_a}{V}}$$

For a molar solution of acetic acid ($V=1$):

$$\frac{\alpha}{V} = \sqrt{18 \times 10^{-6}} = 0.0042 \text{ gm.-ions per litre.}$$

From the table, p. 197, we see that at such low concentrations the influence of electrical interaction on the mobilities of the ions is almost negligible.

Examples: (i) A weak electrolyte is 2 per cent dissociated in N/10 solution. Calculate its degree of dissociation in a hundredth-normal solution.

$$\frac{\alpha^2}{V} = \text{a constant,}$$

$$\therefore \frac{\alpha^2}{V} = \frac{\alpha'^2}{V'}$$

$$\therefore \frac{2^2}{10} = \frac{\alpha'^2}{100}$$

$$\therefore \alpha'^2 = 40,$$

$$\therefore \alpha' = 6.3,$$

\therefore degree of dissociation in N/100 solution is 0.063, or 6.3 per cent.

(ii) A certain monobasic organic acid is a weak electrolyte. Its degree of dissociation at a dilution of 256 is 0.112. Calculate its dissociation constant.

$$K = \frac{a^2}{(1-a)V}, \text{ or roughly, } \frac{a^2}{V}$$

$$= \frac{0.112 \times 0.112}{256}$$

$$= \underline{4.9 \times 10^{-5}}.$$

Transport (or Transference) Numbers. In 1853 HITTORF (1824-1914) began to make experiments on the changes of concentration occurring near the electrodes during electrolysis in a quiescent electrolyte solution. His apparatus is indicated in Fig. 45. Speci-

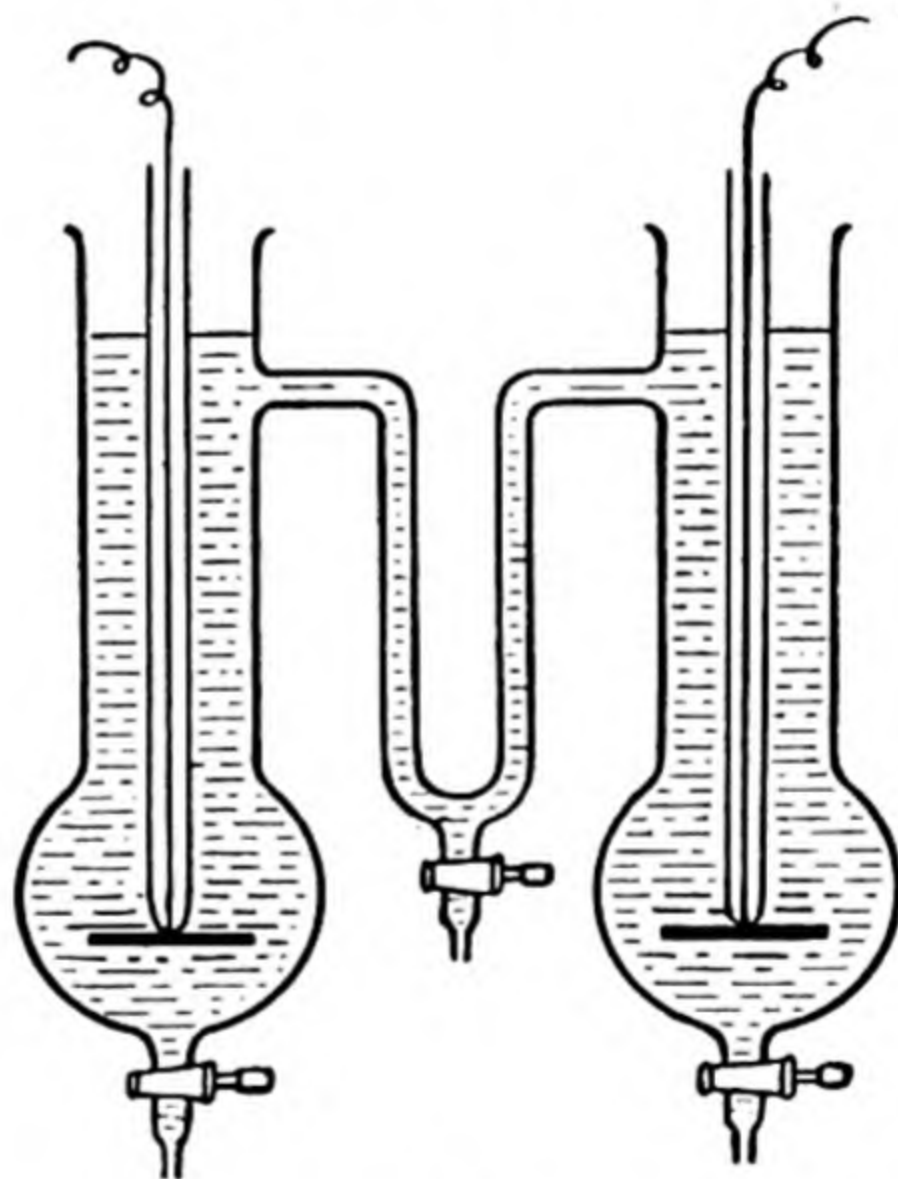


FIG. 45. MODIFIED HITTORF APPARATUS

mens of the solution round each electrode and from the intermediate section of solution could be tapped off and the concentration of electrolyte in them ascertained by suitable chemical methods of estimation. The diagram and following explanation show how these investigations led to a comparison of the speeds of the cations and anions in the electrolyte solution.

In Fig. 46, level (i) shows the state of affairs before the current

is switched on. ● represents an anion and ○ a cation. The cell is divided into three sections by imaginary partitions I and II. The compartment to the left is the anode chamber, and that to the right is the cathode chamber.

Suppose that the anions and the cations both move at the same speed; that the current is passed; and that in a given time 3 anions

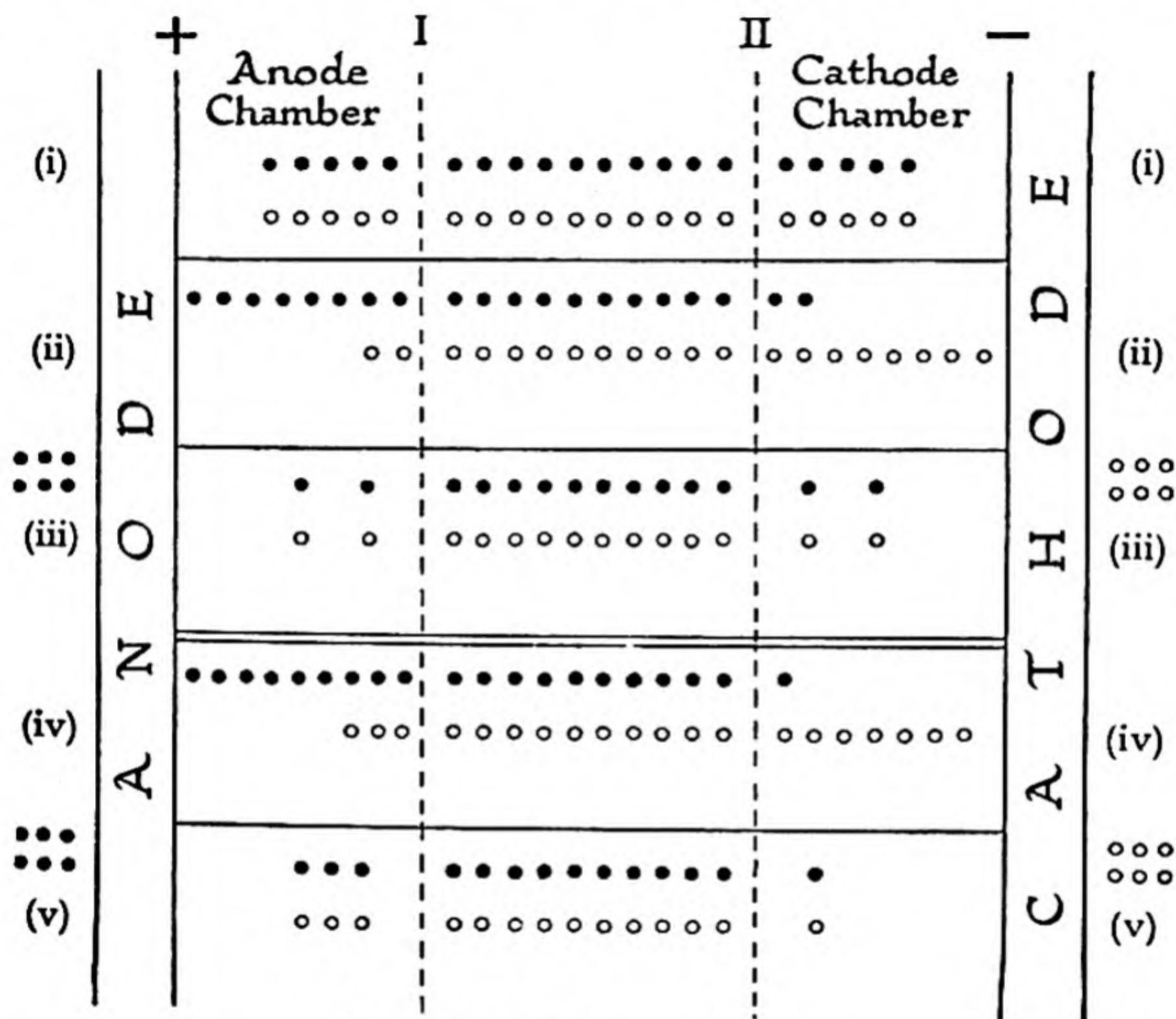


FIG. 46. MIGRATION OF IONS

have crossed from the middle chamber to the anode chamber. Then in the same time, since they are assumed to move with equal speed, 3 cations will have crossed from the middle chamber to the cathode chamber (level ii). All unpartnered ions are now to be regarded as discharged at the electrodes (level iii). It will be seen (a) that the number of anions discharged equals the number of cations discharged, and if (as is assumed in this case) both kinds of ions carry the same charge, this must be so whatever their respective speeds, for the solution as a whole would otherwise become charged,

whereas in fact it always remains electrically neutral; (b) that while the solutions in both anode and cathode chambers have become less concentrated, the fall in concentration is the *same* in each, viz. from 10 ions to 4 ions.

Now suppose the anion to move *twice as fast* as the cation. Then if the original state is again as in level (i), the condition when 4 anions have crossed from the middle chamber to the anode chamber will be as shown in level (iv). Two cations will in the same time have crossed into the cathode chamber, and the number of unpartnered ions in both anode and cathode chambers is 6. In level (v) these unpartnered ions are shown as discharged, and the concentrations of the anode and cathode chambers are in the ratio of 6 to 2. That is, the *fall* in concentration round the cathode is from 10 to 2, i.e. 8, while the *fall* in concentration round the anode is from 10 to 6, i.e. 4.

$$\therefore \frac{\text{Fall in concentration round cathode}}{\text{Fall in concentration round anode}} = \frac{8}{4} = 2,$$

which is the ratio of the speed of the anion to that of the cation. In general,

$$\frac{\text{Speed of anion}}{\text{Speed of cation}} = \frac{\text{Fall in concentration in cathode liquid}}{\text{Fall in concentration in anode liquid}}.$$

It should be carefully noted that, while in the second example the anion moved twice as fast as the cation, equivalent weights of substance were nevertheless liberated at the anode and cathode. Since, however, the extra speed of the anion means that it is twice as effective as the cation in leaving unpartnered ions in a given time, we may use a figure of speech and say that '*the anion carries twice as much of the current as the cation does.*' Similarly, if the anion has a speed of $3u$ and the cation a speed of u we say that the anion carries $\frac{3}{4}$ of the current and the cation $\frac{1}{4}$. We thus arrive at the formula

$$\frac{\text{Loss at cathode}}{\text{Loss at anode}} = \frac{\text{Speed of anion}}{\text{Speed of cation}} = \frac{t_-}{1-t_-},$$

where t_- is the fraction of the current carried by the anion and $1-t_-$ is the fraction carried by the cation.

t_- and $1-t_-$ are called the *transport numbers* of the anion and cation respectively.

By transposition of the above equation, it can be shown that

$$t_- = \frac{\text{Loss at cathode}}{\text{Total loss at cathode and anode}};$$

for, let the loss at the cathode be x and that at the anode be y ,

$$\text{then } \frac{x}{y} = \frac{t_-}{1-t_-}, \quad \therefore yt_- = x - xt_-,$$

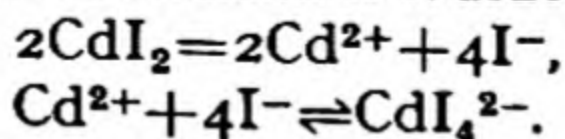
$$\text{or } t_-(x+y) = x; \text{ whence } t_- = \frac{x}{x+y}.$$

So far it has been assumed that no chemical action has occurred at the electrodes; but if such action does take place the difference in treatment can easily be understood. Suppose, in illustration, that copper sulphate is electrolysed between copper electrodes; then at the anode copper dissolves as cupric ions, Cu^{2+} , which partner the incoming sulphate ions. Hence if the SO_4^{2-} ion moves faster than the Cu^{2+} ion, there will actually be a *gain* in concentration of copper in the anode chamber. But the total copper in the whole solution will remain constant, therefore in the cathode chamber there must be a *loss* of copper equal to the gain in the anode chamber. At the same time, the *total* loss in copper which would have taken place under the same conditions, if no replacement had been made from the anode, is given by the weight of copper deposited on the cathode.

$$\text{That is, } t_- = \frac{\text{Gain in concentration of copper round anode}}{\text{Weight of copper deposited on cathode}}.$$

If the gain or loss in concentration in the anode or cathode chambers is given in terms of some substance different from that in which the total loss is expressed, these various weights must be converted into fractions of gram-ions before the calculation is made. This will be illustrated in some of the examples which follow.

Investigation of Complex Ions. Hittorf's method found very important applications in proving the existence and formulae of *complex ions* (p. 110). For example, it was shown that in solutions of potassium ferrocyanide, $\text{K}_4\text{Fe}(\text{CN})_6$, or potassium ferricyanide, $\text{K}_3\text{Fe}(\text{CN})_6$, iron moved exclusively to the *anode*, at all concentrations, and was contained in stable anions, of formulae $\text{Fe}(\text{CN})_6^{4-}$ and $\text{Fe}(\text{CN})_6^{3-}$ respectively (see Example (vii), p. 213). In dilute solutions of cadmium iodide, CdI_2 , the metal migrated normally to the cathode, but in concentrated solutions it travelled *both to the cathode and anode*. Such an apparent paradox received a simple explanation as follows: the ionization of cadmium iodide proceeds in two stages:



Hence in concentrated solution the principal ions are Cd^{2+} and the complex anion CdI_4^{2-} , but in dilute solution the complex is almost totally dissociated. In the anion CdI_4^{2-} iodine is bound to the

cadmium ion Cd^{2+} by co-ionic links (p. 108) made possible by vacant orbitals in the cation. Such complexes are common in aqueous solutions of the halides of the heavier metals. Since the ligands of the complex ion are supplied by the salt itself they are often termed *auto-complexes*. The well-known colour change in cupric chloride solution from green to blue as it is diluted is mainly due to the dissociation of the *yellow* anion CuCl_4^{2-} to the blue simple cation Cu^{2+} and the colourless chloride ion. For the formation and constitution of ferro- and ferricyanide ions see p. 594.

The Moving Boundary Method. As a means of determining transport numbers Hittorf's method suffers from serious disadvantages:

(i) Any experiment, leading eventually to only one determination, is extremely protracted. Obviously the heating effect of an electric current, causing interdiffusion of the sections of solution, must be minimized. Hence only currents of a few milliamperes may safely be used. On the other hand, an accurate value of transport number can be expected only when the changes of concentration are sufficient not to overstrain the accuracy of the analyses.

(ii) The method is limited in scope because it necessitates not only the migration of ions through the solution but also their discharge at the electrodes. This process is often not simple: for example, at the anode in a dilute solution of chloride mainly hydroxyl ions are discharged (p. 40). Further, since ions lose their water of hydration on discharge and the degree of hydration varies widely (p. 144), water is transported between the electrodes and the change of concentration is thereby modified.

LODGE (1851-1940) in 1883 and WHETHAM (1867-1952) ten years later initiated experiments in which the transport of ions is visibly demonstrated, and their discharge is not directly involved.

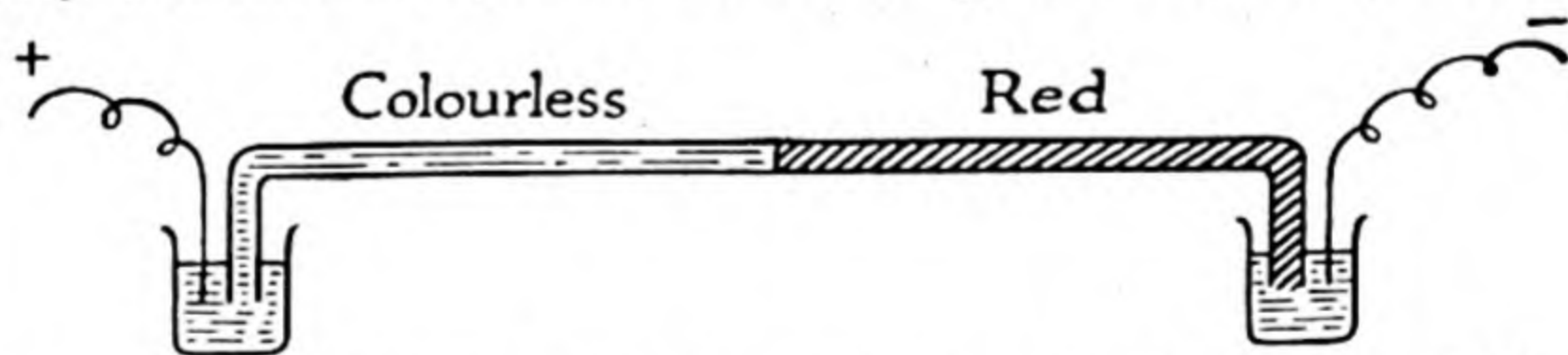


FIG. 47. SIR OLIVER LODGE'S EXPERIMENT ON IONIC MIGRATION

Lodge's method of experiment was as follows. In a warm solution of sodium chloride, containing a trace of alkali and coloured pink by the indicator phenolphthalein, gelatine was dissolved, and the whole solution poured into a long bent tube, as shown in Fig. 47. After the gelatine had set, the tube was inverted so that the bent ends each dipped into dilute sulphuric acid. On connecting electrodes

in the acid to a battery, hydrogen ions moved slowly through the solution from the positive to the negative pole, decolorizing the indicator as they progressed. Such early semi-quantitative experiments demonstrated for the first time the very low velocity of migration of even the fastest cation. It was later shown that the presence of gelatine had little, if any, effect on the velocity.

In a modern form of Whetham's apparatus (Fig. 48) the anode,

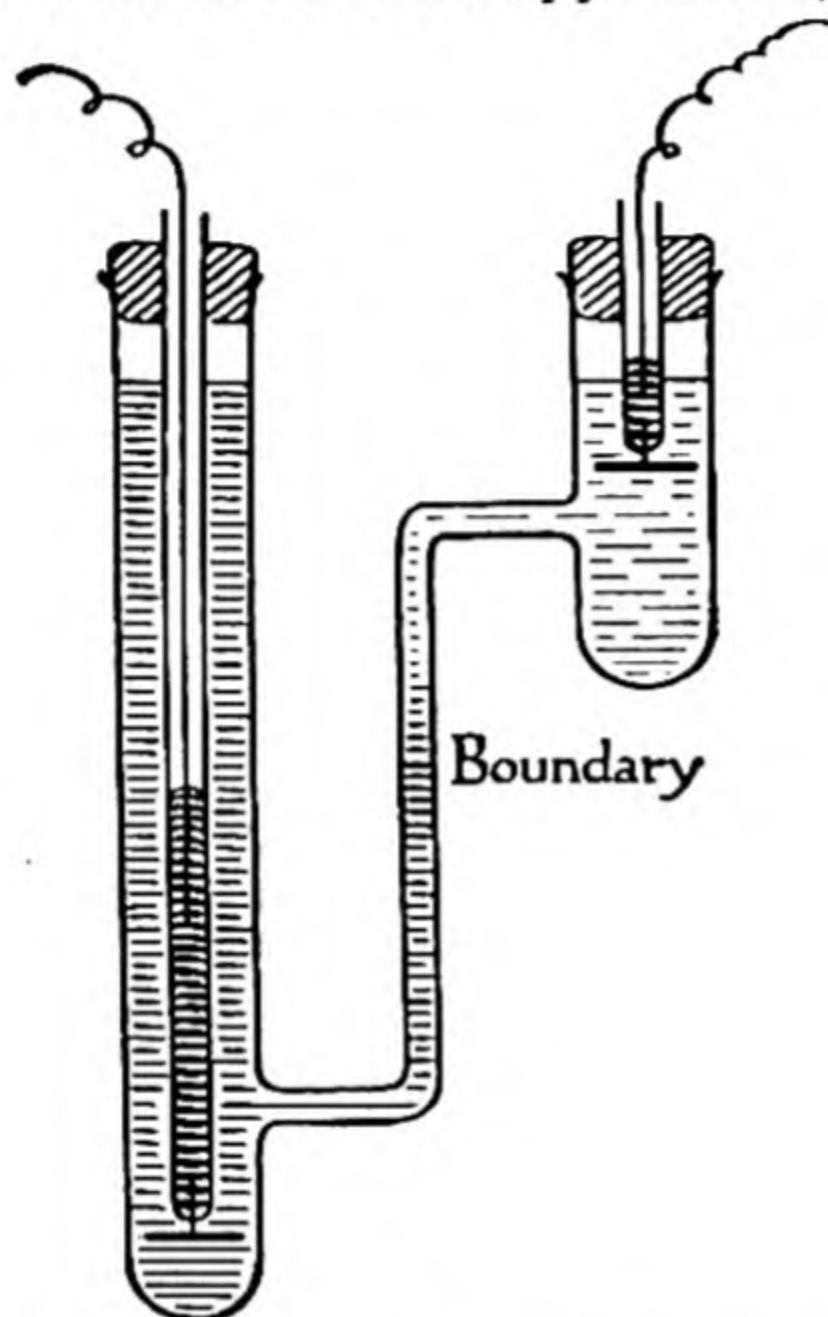


FIG. 48. DIRECT DETERMINATION OF IONIC VELOCITIES

placed in the longer vessel, is of pure cadmium. The tube connecting the electrodes is of uniform bore (diameter about 2 mm.) and graduated in 0.1 c.c. Both vessels and the connecting tube are first filled with a dilute chloride solution, e.g. 0.1 N hydrochloric acid, coloured blue by the addition of a trace of the indicator methyl violet. On passing a small current cadmium chloride, CdCl_2 , is produced at the anode and its colourless solution travels into the capillary tube, there forming with the blue acid solution a sharp boundary, which moves slowly up the tube.

Suppose that in a particular experiment with 0.1 N hydrochloric acid the boundary is observed to sweep out a volume of 0.1 c.c. in 387 seconds, while the current is constant at 0.003 amperes. In

this time all the hydrogen ions originally in this volume must have migrated upwards (while the chloride ions move downwards towards the anode). Now 0.1 c.c. of the electrolyte contains 10^{-5} gm.-ions of hydrogen, with total charge $96,500 \times 10^{-5}$ coulombs. The current carried by this ion is therefore $i_+ = \frac{0.965}{387} = 0.00249$ amp. The total current is 0.003 amp. Hence $\frac{i_+}{i} = t_+ = \frac{0.00249}{0.003} = 0.83$, and $t_- = 1 - 0.83 = 0.17$.

It should be carefully noted that the transport number is not a specific property of an ion, for it depends on the ion completing the electrolyte. For example, while in HCl the transport number of chloride ion is only 0.17, in KCl, the ions of which move at nearly equal speeds, it is 0.503.

Ionic Mobilities and Ionic Speeds. From p. 206 and p. 194 we have:

$$\frac{t_-}{1 - t_-} = \frac{\text{speed of anion}}{\text{speed of cation}} = \frac{u_-}{u_+},$$

$$\text{whence } t_- = \frac{u_-}{u_+ + u_-} = \frac{Fu_-}{Fu_+ + Fu_-} = \frac{\lambda_-}{\Lambda},$$

$$\text{and } 1 - t_- = t_+ = \frac{Fu_+}{Fu_+ + Fu_-} = \frac{\lambda_+}{\Lambda}.$$

Thus if the transport number t of an ion is determined in an electrolyte at dilution V , and the equivalent conductance of the electrolyte is found at the same dilution, we can at once calculate the mobility of the ion from the relation

$$(\lambda)_V = \Lambda_V \times t,$$

or, in words,

mobility of an ion = equivalent conductance of electrolyte \times transport number of the ion in that electrolyte.

Mobilities are, however, usually quoted for 'infinite' dilution: for HCl, $\Lambda_\infty = 379.4$ mhos, and $t_+ = 0.83$. Hence the mobility of hydrogen ion at 'infinite' dilution is $379.4 \times 0.83 = 315$ (coulombs-cm./sec.).

Mobilities at 18° and Infinite Dilution

H ⁺	315	$\frac{1}{2}$ Mg ²⁺	45	OH ⁻	174
Li ⁺	33	$\frac{1}{2}$ Ba ²⁺	55	Cl ⁻	65
Na ⁺	43			NO ₃ ⁻	62
K ⁺	64			$\frac{1}{2}$ SO ₄ ²⁻	68

The mobility of an ion, being the product of one faraday and its speed in cm./sec. in a field of 1 volt/cm., is the velocity of its trans-

port of electrical charge per equivalent of the ion per cm. per sec. If therefore the mobility is divided by 96,500 (coulombs) the result is the speed of the ion in cm./sec. in that field.

Speeds of Ions at 18° and Infinite Dilution
(cm./sec. for 1 volt per cm.)

H ⁺	0.00326	OH ⁻	0.0018
Li ⁺	0.000342	Cl ⁻	0.000674
Na ⁺	0.000446	NO ₃ ⁻	0.000642
K ⁺	0.000663		

The following points may be noted:

- (i) The general slowness of the drift speeds, and the *relatively* high speeds of hydrogen and hydroxyl ions.
- (ii) At a given temperature the speed of drift of an ion can depend only on its size and charge, in addition to the strength of the electric field. We conclude that the order of size of the dissolved alkali-metal ions is $\text{Li}^+ > \text{Na}^+ > \text{K}^+$, but the table on p. 144 shows that in crystals containing these ions this order is reversed. In this contrast there is further proof that ions are hydrated in solution, and that the smaller the ion the more water it attracts and binds. In fact the small lithium ion attracts and holds so much water that it becomes larger than the hydrated potassium ion and travels only about half as fast.

Examples: (i) The ionic mobilities of potassium and hydroxyl ions are 64.6 and 174 respectively. Calculate the equivalent conductance of potassium hydroxide at infinite dilution.

Equivalent conductance of KOH at infinite dilution, Λ_∞ ,

$$= \lambda_A + \lambda_K = 64.6 + 174 = \underline{238.6}.$$

(ii) The equivalent conductance of a N/32 solution of a weak acid is 9.2 reciprocal ohms. If the equivalent conductance at infinite dilution is 389 reciprocal ohms, what is the dissociation constant of the acid?

$$\frac{\Lambda_v}{\Lambda_\infty} = \alpha = \frac{9.2}{389}, \text{ where } \alpha \text{ is the degree of dissociation.}$$

But the dissociation constant, K , is by Ostwald's Law equal to

$$\frac{\alpha^2}{(1-\alpha)V}.$$

$$\text{Hence } K = \frac{\left(\frac{9.2}{389}\right)^2}{\left(1 - \frac{9.2}{389}\right)^{32}}, \text{ since the dilution is 32.}$$

$$\therefore K = \underline{1.79 \times 10^{-5}}.$$

(iii) At 20°C . the mobility of the sodium ion is 43.4 and that of the nitrate ion is 61.8. Calculate (a) the equivalent conductance of sodium nitrate at infinite dilution, and (b) the transport numbers of the sodium and nitrate ions.

$$\begin{aligned} \text{(a) Equivalent conductance at infinite dilution} \\ = 43.4 + 61.8 = \underline{105.2 \text{ mhos.}} \end{aligned}$$

(b) Transport number of the sodium ion

$$\begin{aligned} &= \frac{43.4}{43.4 + 61.8} \\ &= \underline{0.41.} \end{aligned}$$

\therefore transport number of nitrate ion

$$\begin{aligned} &= 1 - 0.41. \\ &= \underline{0.59.} \end{aligned}$$

(iv) In the electrolysis of a solution of copper sulphate, by a current of 1.0 amperes for 45 minutes, the anode liquid gained 0.5321 gm. copper and the cathode liquid lost the same weight. Calculate the transport number of copper for this solution. (1 coulomb deposits 0.000329 gm. copper.)

$$\begin{aligned} \text{Weight of copper deposited at cathode} \\ = 45 \times 60 \times 0.000329 \\ = 0.8883 \text{ gm.} \end{aligned}$$

\therefore transport number of sulphate ion

$$\begin{aligned} &= \frac{\text{fall in concentration of copper round cathode}}{\text{total fall in concentration of copper}} \\ &= \frac{0.5321}{0.8883} = 0.599. \end{aligned}$$

\therefore transport number of copper ion

$$= 1 - 0.599 = \underline{0.401.}$$

(v) In the electrolysis of a solution of hydrochloric acid between cadmium electrodes the following results were obtained: gain in chlorine round the anode and loss in chlorine round the cathode, 0.00665 gm.; silver deposited in a voltameter in series with the cell, 0.1190 gm. Find the transport numbers of the hydrogen and chlorine ions. ($\text{Cl}=35.5$; $\text{Ag}=108$.)

Loss of gram-ions of substance (here chlorine) round cathode

$$= \frac{0.00665}{35.5}$$

Total weight of substance (here silver) deposited in the voltameter $= \frac{0.1190}{108}$ gm.-ions; and this must be equal to the total loss in the cell, in gram-ions.

$$\therefore t = \text{transport number of chlorine ion} = \frac{\frac{0.00665}{35.5}}{\frac{0.1190}{108}} = 0.17.$$

$$\therefore 1 - t = 0.83.$$

\therefore transport numbers are: hydrogen, 0.83; chlorine, 0.17 (cf. Moving Boundary Method, p. 210).

(vi) The transport number of the chlorine ion in a decinormal solution of sodium chloride is 0.62. The equivalent conductance of sodium chloride at infinite dilution is 108.9 mhos. Calculate the ionic mobilities of sodium and chlorine ions.

$$\frac{t_-}{1 - t_-} = \frac{\lambda_-}{\lambda_+}$$

$$\therefore \frac{\lambda_-}{\lambda_+} = \frac{0.62}{0.38}, \quad \therefore \lambda_- = \frac{0.62\lambda_+}{0.38}$$

$$\text{But } \Lambda_\infty = \lambda_- + \lambda_+ = 108.9$$

$$\therefore \frac{0.62\lambda_+}{0.38} + \lambda_+ = 108.9$$

$$\therefore \lambda_+ = 41.4$$

$$\therefore \lambda_- = 108.9 - 41.4 = 67.5.$$

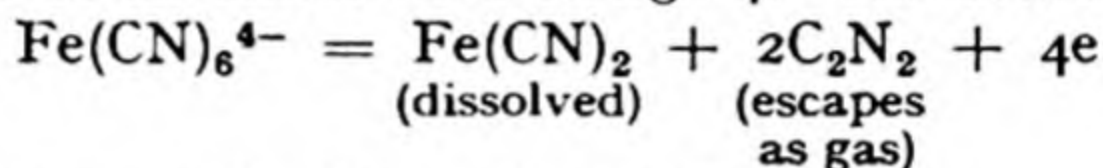
\therefore Ionic mobilities are: sodium, 41.4; chlorine, 67.5.

(vii) After the electrolysis of a solution of potassium ferrocyanide, $\text{K}_4\text{Fe}(\text{CN})_6$, in Hittorf's apparatus, with platinum

electrodes, the anode compartment was found to contain in solution 1.4585 gm. of potassium and 0.6009 gm. of iron. During the electrolysis 0.00521 gm.-atoms of silver were dissolved from the silver anode in a voltameter in series with Hittorf's apparatus. Show that these results agree with the formulation $(K^+)_4.Fe(CN)_6^{4-}$ for potassium ferrocyanide.

In potassium ferrocyanide 1.4585 gm. of potassium is combined with $1.4585 \times \frac{55.85}{4 \times 39.1} = 0.5281$ gm. of iron. Hence the anode compartment contained $0.6009 - 0.5281 = 0.07285$ gm. of iron, that is $\frac{0.07285}{55.84} = 0.00130$ gm.-atom of iron, in excess.

Since $\frac{\text{gm.-atom of silver dissolved}}{\text{gm.-atom of iron in excess}} = \frac{0.00521}{0.00130} = 4$, one gm.-atom of iron must have entered the anode solution during the discharge of an anion with charge 4. An anode reaction



is in harmony with these observations.

CHAPTER XVII

ACIDS, BASES, AND SALTS

Historical. The chemical notions conveyed by the terms *acid* and *base*, which were already important in eighteenth-century chemistry, have steadily gained precision as chemical knowledge and insight developed during the past century and a half. In 1744 the eminent French chemist G.-F. ROUELLE used the term *base* which he regarded as including the following classes of substance:

Bases	Alkalis	Soda and potash (sodium and potassium carbonates). These were easily fusible and soluble in water. Volatile alkali (ammonia).
	Earths	Magnesia and lime, which were infusible and sparingly soluble in water.
	Calces	Calces were the products of 'calcining,' or roasting, metals in air (copper oxide, zinc oxide, iron oxide, etc.). They were both infusible and insoluble in water.

Acids were regarded as substances acting upon a base to give bodies called *salts*, in which the characteristic properties of both acid and base had in general disappeared; the acid and base were therefore said to *neutralize* each other. LAVOISIER, in 1777, noticed that certain elements, such as carbon, phosphorus, or sulphur, produced not bases but acids on combustion in the gas named 'vital air' by its discoverers SCHEELE and PRIESTLEY (1771-4). The name 'oxygen' was given to the gas to connote his conception that it was the essential generator of acids.* BERTHOLLET (whose views on constancy of composition are referred to on p. 17) proved in 1787 that 'prussic acid' (modern hydrocyanic acid, HCN) contained only hydrogen, carbon, and nitrogen; and 'hydrosulphuric acid' (modern H₂S) only hydrogen and sulphur. Between 1810 and 1813 DAVY demonstrated, as contributing to his proof of the elementary nature of chlorine, that no oxygen could be detected in hydrochloric acid, then known as 'oxymuriatic acid,' and in 1815 he proposed that *hydrogen* and not oxygen is the essential constituent of acids.

* Greek, *oxus*, sour; and *gennao*, produce.

Four years later BERZELIUS published an account of his 'dualistic theory' based upon the facts of electrolysis (p. 11). The theory led him to formulate salts as compounds of oxides, e.g. $\text{Na}_2\text{O}.\text{SO}_3$, $\text{CaO}.\text{CO}_2$, the one a base (with supposed net positive charge) and the other an acid (with net negative charge), and, being widely accepted until nearly the middle of the nineteenth century, fostered a long-enduring confusion between *acid anhydride* and true acid. In dealing with very complicated naturally occurring salts mineralogists have found it profitable to perpetuate Berzelius's nomenclature to the present day. LIEBIG, in 1838, took the first step towards a modern outlook by proposing to define acids as *compounds containing hydrogen replaceable by metals*. It was not until fifty years later that ARRHENIUS, inspired by his theory of ionization in aqueous solution, could assert that a compound yielding *hydrogen ions* in solution was an *acid*, and one producing *hydroxyl ions* a *base*.

While it could not be assumed that all the hydrogen atoms in a molecule of an acid were replaceable by a metal (e.g. $\text{H}.\text{C}_2\text{H}_3\text{O}_2$, acetic acid), it was recognized that many acids gave rise to more than one distinct series of salts: sulphuric acid gave NaHSO_4 and Na_2SO_4 ; phosphoric acid gave NaH_2PO_4 , Na_2HPO_4 , and Na_3PO_4 , while nitric acid afforded only NaNO_3 . Because in producing such salts acids necessarily reacted with 1, 2, 3, etc. equivalents of the base NaOH , they were classified as *monobasic* (hydrochloric, nitric, acetic, etc.), *dibasic* (sulphuric, oxalic, etc.), *tribasic* (phosphoric), and so on. Conversely, *bases*, reacting with no more than one molecular weight of a monobasic acid, were styled *monacid* (e.g. ammonia); if twice this amount of acid was required the base was *di-acid* (calcium hydroxide), and if three times it was *tri-acid* (aluminium hydroxide). This terminology of the *basicity* of acids and the *acidity* of bases has survived to the present day, although in the light of modern views it could easily lead to confusion.

The Ionization of Water. Although water is an extremely weak electrolyte, its ionization plays a fundamental part in the electrolysis of many aqueous salt solutions (p. 39), as well as in the general theory of acids and bases. Since the presence of even small amounts of dissolved carbon dioxide or of traces of salts may cause the apparent electrical conductance of water to rise to many thousand times the conductance of the pure substance, its purification before determining the true conductance is very exacting. In 1894 KOHLRAUSCH and HEYDWEILLER, after numerous distillations *in vacuo* in a platinum apparatus, finally obtained a specimen of water with specific conductance 0.043×10^{-6} mho, at 18° , which was not reduced after further distillation; the specific conductance of ordinary distilled water is $5 - 10 \times 10^{-6}$ mho.

The degree of dissociation, α , is the (fractional) number of gm.-

ions of hydrogen (or hydroxyl) from one gm.-molecule of water: or from one gm.-equivalent of water, since both are the same.

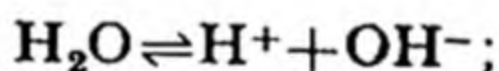
$$a = \frac{\Lambda}{\Lambda_{\infty}},$$

where Λ_{∞} is the sum of the limiting mobilities of hydrogen and hydroxyl, that is $\Lambda_{\infty} = 315 + 174 = 489$, at 18° (p. 202), and Λ = the equivalent conductance = specific conductance (κ) \times vol. (V) in c.c. containing 1 gm.-equivalent (or 1 gm.-molecule) of water (p. 194).

Therefore $a = \frac{\kappa V}{489}$, or $\frac{a}{V} = \frac{\kappa}{489}$, where $\frac{a}{V}$ is the concentration in gm.-ion *per c.c.*, of hydrogen or hydroxyl ions in water. Accordingly this concentration is (at 18°):

$$\begin{aligned} & \frac{0.043 \times 10^{-6}}{489} \\ &= 0.88 \times 10^{-10} \text{ gm.-ion per c.c.} \\ &= 0.88 \times 10^{-7} \text{ gm.-ion per litre.} \end{aligned}$$

If we symbolize the hydrogen ion as H^+ we have for the equilibrium:



on applying the law of mobile equilibrium,

$$\frac{(H^+)(OH^-)}{[H_2O]} = K,$$

where *parentheses* mean 'activity of' (p. 200). Since the degree of dissociation is so small (1) the concentration of water, $[H_2O]$, is effectively constant, (2) the activity coefficients of the ions may safely be taken as unity.

Hence

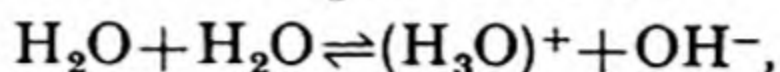
$$[H^+][OH^-] = K_w = (0.88 \times 10^{-7})^2 = 0.75 \times 10^{-14} (\text{gm.-ion/litre})^2.$$

It will be shown later (p. 221) that the heat of formation ΔH of water from its ions, $H^+_{aq.} + OH^-_{aq.} = H_2O$, is approximately -13.5 kcal. Hence the converse process is highly endothermic, and by Le Chatelier's principle the degree of ionization must increase rapidly with rise of temperature:

	25°	50°	100°
$K_w \times 10^{14}$	1.04	5.50	51.3

The importance of the quantity K_w , termed the *ionic product for water*, is that in all dilute aqueous solutions this product must retain its value appropriate to the temperature, however disparate the individual ionic concentrations may become by the presence of dissolved acids or bases.

The hydrogen ion in water being in actuality $(\text{H}_3\text{O})^+$, the ionic dissociation of water is to be represented as

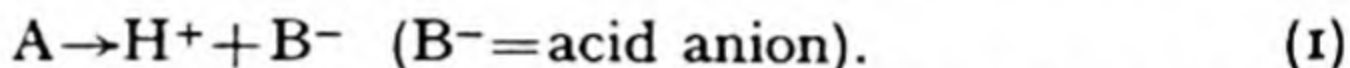


that is, by the transfer of a proton from one molecule to another in contact with it. This more realistic view does not, however, affect the reasoning given above.

Acids and Bases. (N.B. It is to be taken that the solutions discussed in the following sections of this chapter are sufficiently dilute for the assumption that activity coefficients are unity to be a close approximation.)

The few acids and bases which in aqueous solution behave, like salts, as strong electrolytes—e.g. hydrochloric, nitric, and perchloric acids; sodium and potassium hydroxides—are not typical of these classes of chemical compounds, in spite of their importance and long familiarity. We shall therefore consider first the great majority of acids and bases, which being weak electrolytes and partaking in definite chemical equilibria in solution are termed *weak acids* and *weak bases*.

An *acid* A is a *proton donor*, i.e. it is capable of the type of ionization



In the absence of a solvent, such a dissociation, like all ionization under such conditions, would be very highly endothermic and proceed to only a negligible degree. In the presence of *water* as solvent the further reaction



is extremely rapid, far-reaching, and highly exothermic. An equilibrium



can consequently be established in this solvent.

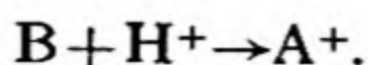
By applying the law of mobile equilibrium to (3) in dilute solution we have:

$$\frac{[\text{H}_3\text{O}^+][\text{B}^-]}{[\text{A}][\text{H}_2\text{O}]} = K; \quad \frac{[\text{H}_3\text{O}^+][\text{B}^-]}{[\text{A}]} = K_a,$$

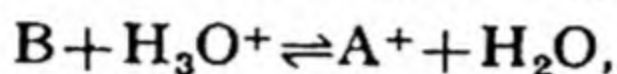
since in such a solution water will be in such excess that its concentration can be taken as constant. The *strength* of the acid A is taken as measured by the *acidic dissociation constant* K_a , which is independent of both degree of dissociation and of dilution. If the solution contains no acid other than A and no other source of anions B^- (such as a salt of acid A), then $[\text{H}_3\text{O}^+] = [\text{B}^-]$, and we have:

$$[\text{H}_3\text{O}^+]^2 = [\text{Acid}] \cdot K_a.$$

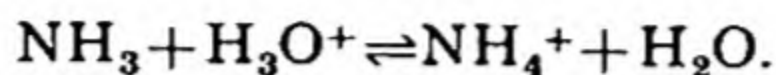
A *base* is a *proton acceptor*, i.e. it is capable of the type of combination



In aqueous solution this reaction takes the form of an equilibrium



for example,



From an early period acids and bases have been regarded as antithetical in action (see previous historical notes), and this modern view gives due prominence to that conception.

Bases were viewed by Arrhenius as compounds that in solution could release a hydroxyl ion, OH^- . This attitude is not essentially contradicted by the present-day theory, for if hydrogen ions are removed from an aqueous medium hydroxyl ions must be left unpartnered.

For the equilibrium involving ammonia shown above we have in dilute solution ($[H_2O]$ constant):

$$\frac{[NH_4^+]}{[NH_3][H_3O^+]} = K'.$$

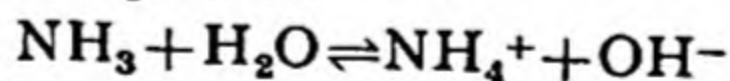
Now in all aqueous solutions $[H_3O^+] = \frac{K_w}{[OH^-]}$.

Hence
$$\frac{[NH_4^+][OH^-]}{[NH_3]} = K' \cdot K_w = K_b,$$

or in general for the base B,

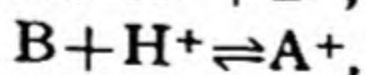
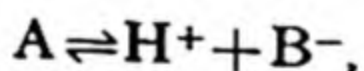
$$\frac{[BH^+][OH^-]}{[B]} = K_b.$$

This is an expression analogous in form to that for the acidic dissociation constant K_a , and is usually taken as a measure of the *strength* of the base B. It is often called the *basic dissociation constant*, but from the equation



it will be seen that it is *water* that is dissociated, and not ammonia. Under conditions parallel to those for a solution of acid A we have $[BH^+] = [OH^-]$ and $[OH^-]^2 = [Base] \cdot K_b$.

Ions as Acids and Bases. The definitions of acid A and base B, viz.:



obviously imply that the anion B^- is a *base*, and the cation A^+ is an *acid*; for example, acetate ion $C_2H_3O_2^-$ is an *anion-base*, and ammonium ion NH_4^+ is a *cation-acid*.

For acetic acid $\frac{[\text{HAc}]}{[\text{Ac}^-][\text{H}_3\text{O}^+]} = \frac{1}{K_a}$, and therefore

$$\frac{[\text{HAc}][\text{OH}^-]}{[\text{Ac}^-]} = \frac{K_w}{K_a} = K_b,$$

where K_b is the basic dissociation constant for *acetate ion*.

For ammonia $\frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = K_b$, and therefore

$$\frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} = \frac{K_w}{K_b} = K_a,$$

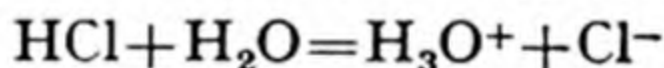
where K_a is the acidic dissociation constant for *ammonium ion*.

Every weak acid, with dissociation constant K_a , has its *conjugate* or *corresponding base* with constant $\frac{K_w}{K_a}$. Conversely, every weak

base with constant K_b has its *conjugate acid* with constant $\frac{K_w}{K_b}$.

The product (strength of acid) (strength of base), where acid and base are conjugate, is the constant K_w . Hence if an acid (or base) is relatively strong, the conjugate anion-base (or cation-acid) is correspondingly weak.

Strong Electrolytes as Acids and Bases. Completely anhydrous liquid *hydrogen chloride* is a non-conductor of electricity and attacks neither carbonates nor metals, but on solution in water the reaction



occurs to completion. The aqueous solution is thus rightly termed *hydrochloric acid*. It follows that the anion Cl^- in aqueous solution has no basic properties (cf. acetate anion, above). Owing to the completeness of their conversion to hydrogen ion and a (neutral) anion such acids as hydrochloric, nitric, and perchloric are termed *strong acids*. In solvents other than water their character as strong electrolytes may not be sustained; for example, in acetone or ethanol solution nitric acid behaves as a weak acid, in definite equilibrium with its ions.

The hydroxides of the alkali-metals, e.g. NaOH and KOH , are termed *strong bases*, and resemble their salts in being ionic crystals, e.g. Na^+OH^- . In aqueous solution the alkali-metal cation is neutral (cf. ammonium ion).

The neutralization of a strong base by a strong acid, e.g.



evidently reduces to



Hence the heat of neutralization, which may readily be determined calorimetrically, is independent of the strong acid or base used. For the neutralization of sodium hydroxide (in 'molar' solution) by acids (also in 'molar' solution) the following heats of reaction per gm.-molecule of acid have been obtained:

HCl	HNO ₃	HClO ₄	
13.79	13.61	13.75	kcal.

Conventional Use of the Symbol H⁺. In the preceding discussion of the modern outlook upon acids and bases it was obviously essential to distinguish explicitly between the *proton* and the hydrogen ion in aqueous solution, H₃O⁺. In solvents other than water similarly *solvated* hydrogen ions exist. On grounds of brevity and simplicity in printing it has become the common convention to designate such actual ions by the simple symbol H⁺, and in the succeeding pages, where no ambiguity can arise, we shall adopt this practice.

Hydrogen-ion Concentration in Aqueous Solutions. A solution which contains the same concentration of hydrogen ion, and therefore of hydroxyl ion, as pure water (at 25°, 10⁻⁷ gm.-ion per litre) is said to be a *neutral* solution, and a substance dissolving to give such a solution is a neutral substance. An *acid* solution is one in which the concentration of hydrogen ion exceeds that of hydroxyl ion, and conversely for an *alkaline* solution. It should be noted that though alkalinity will usually be due to the presence of a *base* the description *alkaline* solution is by convention preferred to the perhaps more logical *basic* solution. Suppose that in a particular acid solution the hydrogen ion concentration is 10⁻⁴; then the hydroxyl ion concentration is 10⁻¹⁴/10⁻⁴ = 10⁻¹⁰ gm.-ions per litre. Similarly, an alkaline solution contains an excess of hydroxyl ions, so that the concentration of hydrogen ions will be less than 10⁻⁷.

To express the state of an aqueous solution with regard to its hydrogen ion concentration, it is inconvenient to use figures which give the actual number of gram-ions per litre, since these numbers are frequently very small. More convenient figures can be obtained by taking the logarithm to base 10 of the gm.-ion/litre concentration and omitting the minus sign. Thus a concentration of 10⁻⁷ gm.-ions of hydrogen per litre is expressed by 7 on this system, and a concentration of 3.7 × 10⁻⁶ gm.-ions of hydrogen per litre by 5.43:

$$\begin{aligned} 3.7 &= 10^{0.57} \text{ (since } 0.57 \text{ is the logarithm to base } 10 \text{ of } 3.7), \\ \therefore 3.7 \times 10^{-6} &= 10^{0.57} \times 10^{-6} \\ &= 10^{-5.43}. \end{aligned}$$

∴ -5.43 is the logarithm to base 10 of 3.7 × 10⁻⁶, and, by removing the minus sign, we get the value 5.43.

Such figures are known as the 'pH value' or the *hydrogen ion exponent* of the solution. The relation between pH and hydrogen ion concentration in gram-ions per litre $[H^+]$ is:

$$\begin{aligned} \text{pH} &= -\log.[H^+] \\ [H^+] &= 10^{-\text{pH}} \end{aligned}$$

Examples: (i) The pH value of a solution is 4.5. What is the concentration of hydrogen ions in it, in gram-ions per litre?

$$\begin{aligned} [H^+] &= 10^{-\text{pH}} \\ &= 10^{-4.5} = 10^{0.5} \times 10^{-5} = 3.16 \times 10^{-5} \end{aligned}$$

(ii) If the pH of a solution is 9.0, how many grams of hydroxyl ions, OH^- , are contained in 1 litre?

The concentration of hydrogen ions $[H^+]$ is 10^{-9} .

$$\begin{aligned} \text{But } K_w &= [H^+] \times [\text{OH}^-] = 10^{-14} \\ \therefore [\text{OH}^-] &= 10^{-14}/10^{-9} = 10^{-5}. \end{aligned}$$

Hence there are 10^{-5} gm.-ions of OH^- per litre; and since 1 gm.-ion of OH^- is 17 gm.,

\therefore there are 17×10^{-5} gm. of OH^- ions per litre.

If the concentration of hydrogen ion is *reduced* to one-tenth, therefore, the pH value is *increased* by 1 unit; and if the concentration is *increased* tenfold, the pH value *falls* by 1 unit. Similar results are obtained by considering solutions of alkalis. In N/10 sodium hydroxide solution, $[\text{OH}^-] = 0.1$ or 10^{-1} ; therefore $[H^+] = 10^{-14}/10^{-1} = 10^{-13}$, and the $\text{pH} = 13$. In N/100 sodium hydroxide $[H^+] = 10^{-14}/10^{-2} = 10^{-12}$, and the pH falls to 12.

It is convenient, especially in calculations, to extend the exponential method of nomenclature to the dissociation constants of weak acids and bases. For acids $\text{p}K_a = -\log_{10} K_a$, and for bases $\text{p}K_b = -\log_{10} K_b$; $\text{p}K_w = -\log_{10} K_w$. In a solution containing only neutral substances besides the acid we have (p. 218):

$$[H^+]^2 = [\text{Acid}] \cdot K_a.$$

$$\text{Therefore } \text{pH} = \frac{\text{p}K_a - \log_{10}[\text{Acid}]}{2}.$$

For most weak acids K_a is small and we may as a good approximation in all but extremely dilute solutions disregard the ionic dissociation in setting down the value of $[\text{Acid}]$; for example in a 0.1 molar solution $[\text{Acid}] = 0.1$. For acetic acid, $K_a = 1.8 \times 10^{-5}$ at 20° , and $\text{p}K = 5 - \log 1.8 = 4.75$.

In decinormal solution:

$$\text{pH} = \frac{4.75 + 1}{2} = 2.88.$$

For a weak base we have the analogous expression

$$[\text{OH}^-]^2 = [\text{Base}] \cdot K_b;$$

and since $\log_{10}[\text{OH}^-] = \text{pH} - \text{p}K_w$

$$\text{pH} = \frac{\log[\text{Base}] - \text{p}K_b}{2} + \text{p}K_w.$$

The basic constant for ammonia is 1.8×10^{-5} at 20° , and $\text{p}K_b = 4.75$; in a decinormal solution

$$\begin{aligned} \text{pH} &= \frac{-1 - 4.75}{2} + 14 \\ &= 11.12. \end{aligned}$$

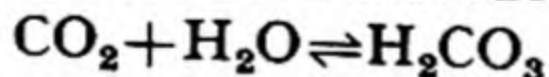
The pH of Natural (Fresh) Water. Normal 'outdoor' air contains a nearly constant proportion of carbon dioxide, amounting to 0.033 volume per cent, i.e. 3.3 litres in 10^4 litres of air. At moderate pressures carbon dioxide, dissolving in water, obeys Henry's Law (p. 145), which may be expressed in the form that the concentration of gas in the saturated solution is proportional to the pressure:

$$[\text{CO}_2]_{\text{aq.}} = a \text{ constant} \times P.$$

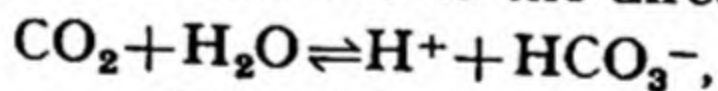
At 15° one litre of water dissolves its own volume of the gas at 1 atmosphere pressure; one litre of gas at this temperature and pressure contains $\frac{1}{23.6} = 0.042$ gm.-mol. (G.M.V. at $15^\circ = 23.6$ litres).

Hence, at 15° , $[\text{CO}_2]_{\text{aq.}} = 0.042P(\text{atm.})$.

In an aqueous solution of carbon dioxide the equilibrium



undoubtedly exists, yielding the relation $[\text{CO}_2] = K[\text{H}_2\text{CO}_3]$, for even in a solution saturated at moderate pressures water is in great excess. The constant K is not known, but we can regard the ionic dissociation of carbonic acid as due to the direct equilibrium



$$\text{giving } \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]} = K_a.$$

The constant K_a has the quite definite value 3.0×10^{-7} (see p. 228), but does not provide a true measure of the strength of carbonic acid, H_2CO_3 . For example, if one out of ten molecules of carbon dioxide were hydrated to the acid, then the true constant would be $10K_a$. Further dissociation of the acid anion HCO_3^- is negligible (p. 237).

In a solution of carbon dioxide in water, $[H^+] = [HCO_3^-]$, and we have

$$\begin{aligned} [H^+]^2 &= [CO_2] \times 3.0 \times 10^{-7} \\ &= P \times 0.042 \times 3.0 \times 10^{-7}; \\ -\log_{10}[H^+] &= pH = 3.95 - \frac{\log_{10} P}{2}; \end{aligned}$$

P (atm.)	pH
1.0	3.95
0.10	4.45
0.001	5.45
0.00033 (air)	5.70

Many waters percolating through fermenting organic matter, such as peat, etc., dissolve amounts of carbon dioxide greatly in excess of that derived from normal air. The acidity of natural waters produced by dissolved carbon dioxide has, over geological time, played a principal part in the weathering of crystalline rocks, and their ultimate conversion into vast masses of sedimentary strata. As we shall discuss later (p. 237), it is also responsible for dissolving calcium compounds, and so enabling aquatic life to originate, by their aggregated shells, the enormous beds of limestone and chalk which exist at the earth's surface.

Acid-base Indicators. The pH of a solution may be determined by electrical methods, but these lie outside the scope of the present book. A simpler method depends upon the fact that various organic compounds, known as *indicators*, undergo definite change of colour when changes in pH occur in solutions containing them. For example, the indicator bromcresol green has a visually unchanging *yellow* colour in solutions up to pH 3.8, and an unchanging *blue* colour in solutions beyond pH 5.4. Between these pH values the observed colour passes through a series of green tints due to the superposition of a decreasing density of yellow on an increasing density of blue. Other indicators have different ranges, and a selection of them may be made to cover the whole range from pH 0 to pH 14, as shown in the table on p. 225.

The pH value of a solution could, then, be determined by observing its effect upon suitably chosen indicators. For instance, a solution in which bromphenol blue remained blue must have a pH not less than 4.6; and if it were also such that bromcresol purple remained yellow in it, the pH cannot be greater than 5.2. Hence the pH lies between 4.6 and 5.2.

By mixing various indicators together, it has been possible to obtain single 'mixed indicators' which show a succession of colour

changes over a very large range of pH. A well-known example is that manufactured by British Drug Houses Ltd.—the *B.D.H. Universal Indicator*. Another type consists of a mixture of methyl orange, methyl red, bromothymol blue, and phenolphthalein; this has the following colours at the pH indicated: red (0–3), orange (4–5), yellow (6), green (7–8), blue (9), violet (10–14)—the spectral order of colours.

Acid-base indicators

	Colour and pH range		pK
Methyl violet	Y (0.1–2.0)	B	—
Thymol blue	R (1.2–2.8)	Y	1.51
Methyl orange	R (3.1–4.4)	Y	3.7
Bromphenol blue	Y (3.0–4.6)	B	3.98
Bromcresol green	Y (3.8–5.4)	B	4.7
Methyl red	R (4.2–6.3)	Y	5.1
Bromcresol purple	Y (5.2–6.8)	V	6.3
p-Nitrophenol	— (5.6–7.6)	Y	7.2
Bromthymol blue	Y (6.0–7.6)	B	7.0
Phenol red	Y (6.8–8.4)	R	7.9
Thymol blue	Y (8.0–9.6)	B	8.9
Phenolphthalein	— (8.3–10.0)	R	9.4
Thymolphthalein	— (9.2–10.6)	B	9.4

Y = yellow: R = red: B = blue:
V = violet: — = colourless.

FIG. 48. INDICATOR TABLE

Theory of Indicators. In general, indicators may be regarded as substances which, in solution, exist in two different forms in equilibrium with one another; they are, in fact, tautomeric compounds like ethyl acetoacetate.* Of the two forms, one is an acid (or a base) while the other is not; hence there is a second equilibrium between the acid (or basic) form and its ions:

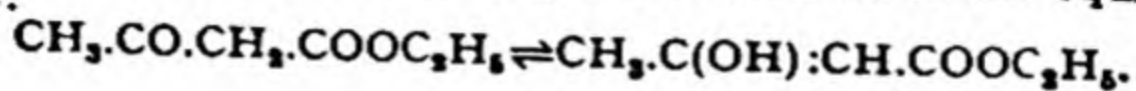
Non-ionizable form \rightleftharpoons acid (or basic) form \rightleftharpoons ions.

All indicators of this type behave as *weak* acids or bases, either because they really are weak, or because the equilibrium

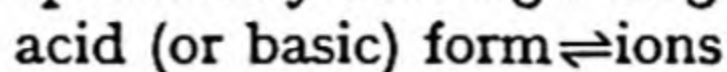
non-ionizable form \rightleftharpoons acid (or basic) form

lies so very largely to the left that, even if the acid (or basic) form is 'strong,' i.e. highly dissociated, very few of the ions exist in plain

* The two forms of ethyl acetoacetate are $\text{CH}_3\text{CO}\cdot\text{CH}_2\cdot\text{COOC}_2\text{H}_5$ and $\text{CH}_3\text{C}(\text{OH})\text{:CH}\cdot\text{COOC}_2\text{H}_5$. Ordinary ethyl acetoacetate is an equilibrium mixture of the tautomers:



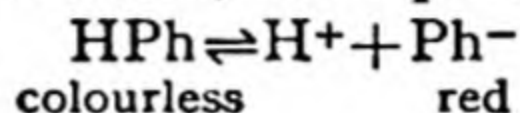
aqueous solution. The argument may therefore be simplified by neglecting the second possibility and regarding the equilibrium



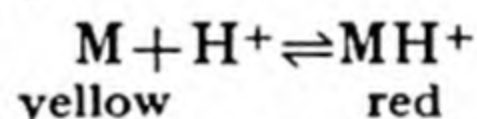
as the equilibrium between a weak electrolyte and its ions.

The next point is that the ions are of a colour different from that of the un-ionized indicator, so that increase or decrease of ionization will finally be marked by a colour change.

As a particular example, let us consider *phenolphthalein*. This behaves as a weak acid, the undissociated molecules being colourless and the anions red. In water, the equilibrium



is set up, HPh representing the undissociated molecule and Ph the anion. On addition of alkali, i.e. hydroxyl ions, the completely ionized salt NaPh is formed, a large increase of the anion Ph⁻ occurs, and its red colour becomes visible. Addition of acid reverses this change, and the colour disappears. Methyl orange functions as a weak base:



Addition of acid, i.e. hydrogen ions, promotes the change to red colour, while addition of OH⁻, by removal of hydrogen ions, reverses that change.

The reason why different indicators change colour at different pH values is that they have different dissociation constants. It can, in fact, be shown that an indicator changes colour round the point where the concentration of hydrogen ions, in gram-ions per litre, is equal to its dissociation constant. Let the indicator be HX, dissociating into H⁺ and X⁻. Then the dissociation constant, K,

is equal to $\frac{[\text{H}^+] \times [\text{X}^-]}{[\text{HX}]}$,

$$\text{or} \quad \frac{[\text{H}^+]}{K} = \frac{[\text{HX}]}{[\text{X}^-]} = \frac{\text{HX}/V}{\text{X}^-/V} = \frac{\text{HX}}{\text{X}^-}.$$

Therefore, when $[\text{H}^+] = K$, that is $\text{pH} = \text{pK}$, equivalent amounts of the two indicator forms HX and X⁻ are present. If HX is yellow and X⁻ is blue the colour will appear as a pure green tint, which may easily be identified as follows. Pour into each of two test-tubes a sample of indicator solution: add to one a drop of aqueous sodium hydroxide and to the other a drop of hydrochloric acid; then view the colour seen on looking through both tubes held one behind the other. Decrease of pH will diminish the amount of X⁻ (blue) and increase that of the form HX (yellow) so that the visible colour becomes yellower. Conversely increase of pH increases X⁻ at the

expense of HX and the colour becomes bluer. Experience shows that with normal acuity of colour-vision the eye detects no further increase of yellow beyond about $\text{pH} = \text{pK} - 1$, and no increase of blue beyond about $\text{pH} = \text{pK} + 1$. Thus the useful range of the indicator for estimation of pH is $\text{pK} \pm 1$, or two units of pH round pK.

Within this range the tint of a *two-colour indicator*, e.g. methyl orange or bromthymol blue, is determined solely by the pH of the solution, and the total amount of indicator is immaterial. With a *one-colour indicator*, e.g. phenolphthalein, there is of course no change of tint but only an increase or decrease of intensity of the same colour. In such a case this intensity is determined not only by the pH but also by the total amount of indicator present.

Buffer Solutions. In preparing such an indicator chart as is given on p. 225, it is necessary that the pH values of the solutions used as standards should be accurately known. Solutions of the kind used in volumetric analysis are quite unsuitable for this purpose, since the presence of even small quantities of impurities may alter their pH very considerably. Thus, suppose we take 50 c.c. of decinormal sodium chloride, in which, since the solution is neutral, the pH is 7. By some accident, a drop (say 0.02 c.c.) of decinormal hydrochloric acid gets into the solution. How is the pH affected?

$[\text{H}^+]$ originally was 10^{-7} ; it is now $\frac{0.02}{50.02 \times 10} = 10^{-4.4}$. That is,

the addition of so little as $\frac{0.02}{10,000}$ gm.-ion of hydrogen has altered the pH value from 7 to 4.4.

A solution will obviously be largely protected against changes of pH through influx of hydrogen (or hydroxyl) ions if it contains both an acid and a base, such as, for example, acetic acid and sodium acetate, the salt providing at its own concentration the conjugate anion-base:

$$\frac{[\text{anion-base}][\text{H}^+]}{[\text{acid}]} = K_a, \text{ or}$$

$$\begin{aligned} \text{pH} &= \text{p}K_a - \log_{10} \frac{[\text{acid}]}{[\text{anion-base}]} \\ &= \text{p}K_a - \log_{10} \frac{[\text{acid}]}{[\text{salt}]} \\ &= \text{p}K_a - \log_{10} \frac{\text{gm.-mol. acid}/V}{\text{G.F.W. salt}/V} \\ &= \text{p}K_a - \log_{10} \frac{\text{gm.-mol. acid}}{\text{G.F.W. salt}} \end{aligned}$$

This derivation shows that for a given ratio of gm.-molecules of acid and G.F.W. of the salt in dilute solution the pH of the solution is independent of its volume.

Small intakes of hydrogen or hydroxyl ion will only slightly increase or decrease respectively the ratio acid/salt. Now it is a well-known fact, easily verified by numerical examples, that for a variable ratio $r = \frac{x}{y}$, r changes least for a given small alteration of x or y when $x = y$. A solution of a given acid and its salt containing equal fractions of a gm.-molecule of the acid and a G.F.W. of salt is termed the *standard buffer solution* for that acid. Its pH is equal to pK_a ($\log_{10} 1 = 0$). Outside the range $r = 0.1 - 10.0$, buffering action ceases to be practically effective, so a combination of a given acid and its salt affords a range of $pH = pK_a \pm 1$ (cf. indicators, above). For acetic acid $pK_a = 4.75$, and hence the *standard acetate buffer* has $pH = 4.75$, and acetate buffers are serviceable in the pH range 3.75–5.75.

In qualitative analysis a buffer mixture of the base ammonia and the conjugate cation-acid ammonium ion NH_4^+ is used as a precipitant of the metals Al, Cr, and Fe (ferric) as hydroxides. By analogy we can write:

$$p(OH^-) = pK_b - \log_{10} \frac{NH_3}{NH_4Cl}$$

where $p(OH^-) = -\log_{10}(OH^-)$. When the base/salt ratio is unity $p(OH^-) = pK_b = 4.75$, and $pH = 14 - 4.75 = 9.25$.

A buffer mixture maintaining the neutral condition ($pH = 7$) is formed by mixing in solution the two salts Na_2HPO_4 and NaH_2PO_4 . These salts yield the *anion-acid* $H_2PO_4^-$ and its conjugate base HPO_4^{2-} at concentrations equal to their own. A dilute solution containing equal fractions of the G.F.W. of the salts has $pH = 6.8$, and another with double as much of the salt Na_2HPO_4 , i.e. of the base HPO_4^{2-} , has $pH = 7.2$.

The Carbonate Buffer. A solution containing definite amounts of sodium hydrogen carbonate, $NaHCO_3$ ('bicarbonate'), and dissolved carbon dioxide is easily produced by adding dilute hydrochloric acid to a cold solution of the bicarbonate, in amounts *insufficient* to react completely with it. On mixing a 0.2 'molar' solution of $NaHCO_3$ with twice its volume of a 0.05 'molar' solution of HCl a buffer solution is produced in which the ratio $Acid/Salt = CO_2/NaHCO_3$ is unity; its pH is found to be 6.53. Hence $pK_a = 6.53$.

$$\frac{[H^+][HCO_3^-]}{[CO_2]} = K_a = 10^{-6.53} = 3.0 \times 10^{-7}.$$

For discussion of relation of dissolved carbon dioxide to carbonic acid see p. 223 above.

A carbonate buffer giving $\text{pH} \approx 7.3$ plays an important part in maintaining human blood in the slightly alkaline condition essential to health; and, with the salt in the form of calcium bicarbonate, $\text{Ca}(\text{HCO}_3)_2$, the pH of the surface waters of the sea is similarly regulated.

The pH of Aqueous Salt Solutions. Salts producible by neutralizing a *strong base* (NaOH , KOH , etc.) with a *strong acid* (HCl , HNO_3 , etc.) dissolve in water to give neutral solutions ($\text{pH} = 7$) since, as explained on p. 220, the ions of such salts are neutral. Salts formed by treating a *weak base* (e.g. NH_3) with a *strong acid* yield *acid* solutions. A decinormal solution of *ammonium chloride* contains the cation-acid NH_4^+ and the neutral anion Cl^- , each at concentrations of 0.1 gm.-ion per litre. The constant K_a for NH_4^+ is $\frac{K_w}{K_b}$ where K_b is the (basic) constant for ammonia (1.8×10^{-5}). Hence $\text{p}K_a = 14 - 4.75 = 9.25$.

$$\begin{aligned}\text{pH} &= \frac{\text{p}K_a - \log_{10}[\text{acid}]}{2} \quad (\text{see p. 222}) \\ &= \frac{(9.25 + 1)}{2} \\ &= 5.12.\end{aligned}$$

Salts formed by the interaction of a *weak acid* and a *strong base* yield *alkaline* solutions, owing to the presence of the anion-base conjugate with the acid. The constant for this base is $\frac{K_w}{K_a}$, where K_a is the constant for the acid. A solution of *sodium benzoate* containing 0.1 G.F.W. per litre contains the anion-base benzoate and the neutral cation Na^+ , each at concentration of 0.1 gm.-ion per litre. The constant K_a for benzoic acid is 6.2×10^{-5} .

$$K_b(\text{benzoate}) = \frac{K_w}{K_a},$$

$$\text{and } \text{p}K_b = 14 - 4.21 = 9.79,$$

$$\begin{aligned}\text{pH} &= \frac{\log_{10}[\text{base}] - \text{p}K_b}{2} + 14 \quad (\text{see p. 223}) \\ &= \frac{-(1 + 9.79)}{2} + 14 \\ &= 8.61.\end{aligned}$$

Owing to the strength of the carbonate ion CO_3^{2-} , as an anion-base, solutions of *sodium* or *potassium carbonates* are very strongly

alkaline, the pH being as high as 11.6 for 0.1 'molar' solutions, which may be taken as also 0.1 molar in the anion-base.

$$\text{pH} = \frac{\log_{10}[\text{base}] - \text{p}K_b}{2} + 14,$$

$$\text{or} \quad 11.6 = \frac{-1 - \text{p}K_b}{2} + 14,$$

whence $\text{p}K_b = 3.8$.

Carbonate ion is thus a stronger base than ammonia, for which $\text{p}K_b = 4.75$.

Salts formed from a *weak base* B and a *weak acid* A yield in solution both a cation-acid and an anion-base, and the pH of the solution depends on which of these is the stronger.

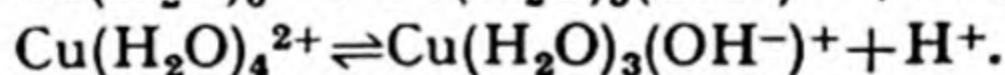
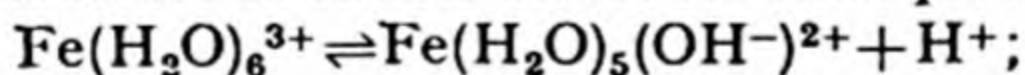
$$K_a \text{ (for cation-acid)} = \frac{K_w}{K_b} \text{ (for the weak base B)}$$

$$K_b \text{ (for anion-base)} = \frac{K_w}{K_a} \text{ (for weak acid A)}$$

We deduce from these relations:

- (i) If the acid A is stronger than the base B ($K_a > K_b$), the anion-base is weaker than the cation-acid, and the solution is *acid* in reaction.
- (ii) In the converse case the solution is *alkaline*.
- (iii) If the base B and the acid A have equal strengths (as in ammonium acetate) the solution will be *neutral*.

Salts of the *heavier metals* containing a (hydrated) cation and a neutral anion (Cl^- , NO_3^- , etc.) usually dissolve to give *acid* solutions, because the cations act as cation-acids: for example:



Use of Indicators in Titration. In volumetric analysis, the object is usually to determine the point at which *chemically equivalent* weights of the reactants have been added to one another. If the problem is the titration of a strong acid against a strong base, this point will be reached when the pH value of the mixed solution is 7; but, as we have just seen, salts of weak acids or weak bases may produce solutions in which the pH is far removed from this value. Hence if, for example, we titrated acetic acid into sodium hydroxide and used bromthymol blue (pH range 6.0–7.6) as indicator, the point at which the indicator changed colour would *not* be the point at which the acetic acid and sodium hydroxide had been added to one another in the ratio of their chemical equivalents. This is because, in sodium acetate solution, there is an excess of

OH^- ions; hence the pH value of the solution of this salt is greater than 7 (in N/10 solution it is, in fact, about 8.9).

It follows that if we run acetic acid solution into sodium hydroxide solution until bromthymol blue changes colour, we shall have added an *excess* of the acid—a sufficient excess, indeed, to bring the pH from 8.9 to 7. Clearly in this titration what we need is an indicator which changes at about $\text{pH}=8.9$, not one which changes at $\text{pH}\approx 7$.

The principles involved in selecting a suitable indicator for a particular acid-base titration may therefore now be considered.

1. *Strong Acid and Strong Base.* In this case, when chemical equivalence has been reached the pH of the solution is 7. It might consequently appear that the indicator used must have a pH range of about 6.5–7.5. That the choice is not thus limited, however, may be seen from the following figures.

Suppose we are titrating N/10 NaOH into 20 c.c. N/10 HCl, and that we have already added 19 c.c. of the alkali. Then 1 c.c. of N/10 HCl will be left in 39 c.c. of the liquid. But 1 c.c. of N/10 HCl contains $\frac{1}{10,000}$ gm.-ion of hydrogen.

$$\therefore [\text{H}^+] = \frac{1}{10,000} \times \frac{1,000}{39} = \frac{1}{39} \times 10^{-1}$$

$$\therefore \text{pH} = 2.6.$$

Now suppose we run in another 0.5 c.c. of the alkali.

$$\text{Then } [\text{H}^+] = \frac{0.5}{10,000} \times \frac{1,000}{39.5} = \frac{0.5}{39.5} \times 10^{-1}$$

$$\therefore \text{pH} = 2.9.$$

On addition of a further 0.45 c.c.,

$$[\text{H}^+] = \frac{0.05}{10,000} \times \frac{1,000}{39.95} = \frac{0.05}{39.95} \times 10^{-1}$$

$$\therefore \text{pH} = \underline{3.9}.$$

But when 20.00 c.c. of the alkali have been added, the only H^+ ions present in the solution will be those of the water itself, and the pH will be 7. That is, the addition of 0.05 c.c. N/10 alkali—about 1 drop—has caused an enormous change in $[\text{H}^+]$ and consequently in pH.

Suppose we continue to run in the alkali. Then if 20.05 c.c. have been added altogether, the $[\text{OH}^-]$ of the solution is

$$\frac{0.05}{10,000} \times \frac{1,000}{40.05} = \frac{0.05}{40.05} \times 10^{-1}$$

$$= 10^{-3.0}$$

$$\begin{aligned}\text{But } [H^+] \times [OH^-] &= 10^{-14}, \therefore [H^+] = \frac{10^{-14}}{10^{-3.9}} \\ &= 10^{-10.1} \\ \therefore \text{pH} &= \underline{10.1}.\end{aligned}$$

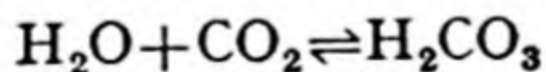
It is plain from these results that, in titrating a strong acid against a strong base, the addition of a very small quantity of acid or base in the immediate neighbourhood of exact neutralization causes a rapid change in the pH value. Hence it does not really matter what indicator is used here. With methyl orange, which changes at about pH 4, the titration reading in the above example would have been 19.95 c.c. instead of 20.00 c.c.; with phenolphthalein, which changes at about pH 8-10, it would have been 20.05 c.c.

2. *Weak Acid and Strong Base.* When a weak acid and strong base are mixed in solution in equivalent proportions, the solution, as we have already seen, contains an excess of OH^- ions, and the pH value is greater than 7, say x . A suitable indicator for such a titration, then, is one which changes colour at $\text{pH} \simeq x$. Thus, in titrating sodium hydroxide with acetic acid, the pH when equivalent quantities have been mixed will be about 9; hence phenolphthalein is a suitable indicator in this case.

3. *Weak Base and Strong Acid.* At chemical equivalence, the pH of the solution made by titrating a strong acid against a weak base is less than 7. For example, the pH of the ammonium chloride solution made by adding 20 c.c. of $N/10HCl$ to 20 c.c. of $N/10$ ammonia is about 5; so that, in titrating these last two solutions against one another, methyl orange or methyl red would give the required end-point.

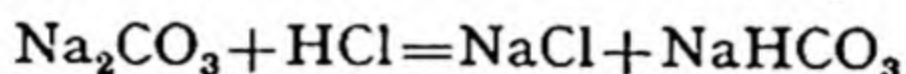
4. *Weak Base and Weak Acid.* In this case the point at which chemical equivalence is reached on titrating the base with the acid cannot be determined by the use of *any* indicator. The changes in $[H^+]$ which occur round the equivalence point are so slowly moving that no sharp end-point is attainable.

5. *Titration of Alkali-Metal Carbonates.* Carbonic acid is by no means a very weak acid. Solutions of it possess, however, a *small* concentration of hydrogen ions, because the equilibrium



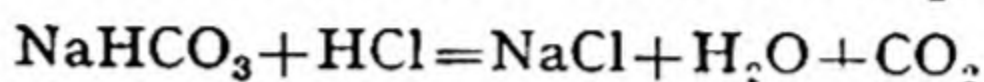
lies preponderatingly to the left. Hence, even if the H_2CO_3 that does exist in the solution is fairly highly ionized, the actual concentration of hydrogen ions is always small. Consequently carbonic acid in effect behaves *as though* it were a very weak acid. Solutions of its salts with strong bases (e.g. Na_2CO_3 and K_2CO_3) have a pH value of at least 10—that is, they are alkaline (see p. 229).

If a solution of hydrochloric acid is run into an unheated solution of sodium carbonate, the pH falls, and it so happens that it becomes about 8 at the point at which *half* the quantity of acid required by the equation $\text{Na}_2\text{CO}_3 + 2\text{HCl} = 2\text{NaCl} + \text{H}_2\text{O} + \text{CO}_2$ has been added. In other words, when the solution has $\text{pH} \approx 8$, the reaction



may be considered to have taken place. This point may be observed in practice by using phenolphthalein as indicator and noting the point at which the red colour is discharged.

On further addition of sufficient acid to complete the reaction



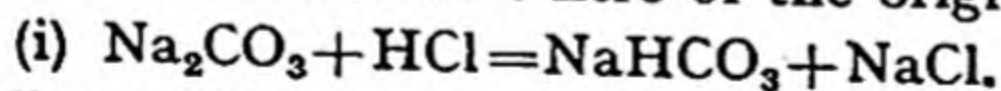
the pH falls further to about 4.5; hence this point may be found by using methyl orange. The acidity of the final solution is due to the presence of carbonic acid (see p. 223). If the carbonate solution is kept hot, being boiled at frequent intervals, the carbonic acid will be decomposed and lost as carbon dioxide, and the final solution will then have a pH of 7.

If the problem is merely an estimation of the concentration of a sodium carbonate solution there is, of course, no need to use phenolphthalein to mark the half-way stage; methyl orange may be used throughout. Suppose, however, that a solution contains both NaHCO_3 and Na_2CO_3 and it is required to estimate the concentration of each. Then, titrating with a standard strong acid, and using phenolphthalein as indicator in the cold, the titration reading will be a measure of the Na_2CO_3 present. If methyl orange is now added and the titration continued, the additional acid required will give the total NaHCO_3 , viz. that originally present, and that formed from the Na_2CO_3 . Hence the weight of each substance may be calculated.

Example: On titrating with N/10 HCl a solution containing sodium carbonate and bicarbonate the following results were obtained:

- (i) Phenolphthalein as indicator: 20 c.c. required 12.2 c.c. acid.
- (ii) Methyl orange as indicator: The solution from (i) required a further 36.2 c.c. acid.

Calculate the weight in grams of (a) sodium carbonate and (b) sodium bicarbonate in 1 litre of the original solution.

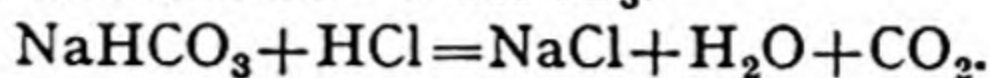


\therefore 1 litre of N/10 acid \equiv 10.6 gm. Na_2CO_3

\therefore 12.2 c.c. of N/10 acid $\equiv \frac{10.6 \times 12.2}{1,000}$ gm. Na_2CO_3

$$\therefore \text{concentration of Na}_2\text{CO}_3 \text{ in solution} = \frac{10.6 \times 12.2}{1,000} \times \frac{1,000}{20} \\ = \underline{6.47 \text{ gm./litre.}}$$

(ii) All the solute is now NaHCO_3 .



\therefore 1 litre of N/10 acid \equiv 8.4 gm. NaHCO_3

$$\therefore 36.2 \text{ c.c. of N/10 acid} \equiv \frac{8.4 \times 36.2}{1,000} \text{ gm. NaHCO}_3$$

\therefore weight of NaHCO_3 which would have been present if 1,000 c.c. of the original solution had been used

$$= \frac{8.4 \times 36.2}{1,000} \times \frac{1,000}{20} \\ = 15.2 \text{ gm.}$$

$$\text{But the original Na}_2\text{CO}_3 \text{ would have given } \frac{6.47 \times 84}{106} \\ = 5.1 \text{ gm.}$$

$$\therefore \text{concentration of NaHCO}_3 \text{ in original solution} \\ = 15.2 - 5.1 = \underline{10.1 \text{ gm./litre.}}$$

The Solubility Product. For the equilibrium between a salt M^+X^- and its saturated solution the law of equilibrium supplies the relation:

$$(\text{M}^+) (\text{Cl}^-) = K,$$

since solid participants in equilibrium may be omitted from the equilibrium quotient (p. 129). In the equation () means 'activity of.' This quite general rule can, however, be usefully applied only when the salt MX is so sparingly soluble that activities of the ions become effectively equal to their concentration, that is, when the activity coefficients f can be taken as unity (p. 200). The solubility of silver chloride at 25° is 1.10×10^{-5} G.F.W. per litre, and for this salt we may confidently assume the relation:

$$[\text{Ag}^+] [\text{Cl}^-] = K = S^2,$$

for when the solvent is pure water:

$$[\text{Ag}^+], \text{ gm.-ion/litre} = [\text{Cl}^-], \text{ gm.-ion/litre} = [\text{AgCl}], \text{ G.F.W./litre} \\ = S, \text{ solubility, in G.F.W./litre.}$$

If the solvent saturated with silver chloride already contained chloride ions (from a soluble chloride), or silver ions (e.g. from silver nitrate) this relation must still hold, because the equilibrium constant K depends only upon temperature. The drastic effect of such conditions on the solubility of silver chloride may easily be

seen as follows. The solubility of silver chloride (G.F.W. 143.4) in water at 25° is 1.58×10^{-3} gm./litre. Hence for the saturated solution we have

$$[\text{Ag}^+] = [\text{Cl}^-] = \frac{1.58}{143.4} \times 10^{-3} = 1.10 \times 10^{-5} \text{ gm.-ion/litre.}$$

If the solvent is 0.01 normal sodium chloride, in which $[\text{Cl}^-] = 0.01$, then since the product $[\text{Ag}^+][\text{Cl}^-]$ must be unchanged, $[\text{Ag}^+]$ and therefore the solubility of AgCl must be reduced by the factor $\frac{1.1 \times 10^{-5}}{10^{-2}}$. The solubility in 0.01 normal sodium chloride is thus:

$$1.58 \times 10^{-3} \times 1.1 \times 10^{-3} = 1.73 \times 10^{-6} \text{ gm./litre,}$$

which is little more than $\frac{1}{1000}$ of its solubility in pure water. The

same effect would, of course, be found by using 0.01 normal silver nitrate as solvent. These are examples of the *common ion effect* and are due to the necessary constancy of the *solubility product* $[\text{Ag}^+][\text{Cl}^-]$. Such a product controls the solubility of all sparingly soluble ionic compounds in the presence of the *common ions*, i.e. ions of which they are themselves constituted. In general, *if in a solution containing ions the concentrations of any pair of these are such that the solubility product of the electrolyte formed from them is momentarily exceeded, precipitation of that electrolyte will take place.*

Examples: (i) With 100 ml. portions of a solution of magnesium sulphate containing 0.2 G.F.W. per litre, 100 ml. portions of a 0.1 molar solution of ammonia containing varying amounts of dissolved ammonium chloride were mixed. It was found that only solutions containing less than 1.00 gm. of ammonium chloride produced a permanent precipitate of magnesium hydroxide on mixing. Calculate the solubility product, $[\text{Mg}^{2+}][\text{OH}^-]^2$. ($\text{NH}_4\text{Cl} = 53.5$: $\text{p}K_b$ for ammonia = 4.75.)

The concentration of ammonium ion in a solution containing 1.00 gm. of NH_4Cl per 100 ml. is $\frac{10.0}{53.5} = 0.187$ gm.-ion per litre.

$$\text{Hence } \frac{\text{NH}_4^+}{\text{NH}_3} = \frac{0.187}{0.10} = 1.87.$$

$$-\log[\text{OH}^-] = \text{p}K_b - \log \frac{\text{NH}_3}{\text{NH}_4^+} \quad (\text{p. 228})$$

$$= 4.75 + \log 1.87 = 5.02.$$

Since the concentration of hydroxyl ion produced by the buffer

is not affected by dilution (p. 228), in the 200 ml. of mixed solution, containing $[\text{Mg}^{2+}] = 0.1$ gm.-ion/litre:

$$[\text{Mg}^{2+}] [\text{OH}^-]^2 = 0.1 \times 10^{-10.04} = \underline{10^{-11}}.$$

(ii) Calculate the solubility of magnesium hydroxide in water, given that its solubility product is 10^{-11} . (Mg=24, O=16.)

In a solution of magnesium hydroxide, $\text{Mg}(\text{OH})_2$,

$$2[\text{Mg}^{2+}] = [\text{OH}^-] \text{ (gm.-ion per litre).}$$

$$\text{Hence } [\text{Mg}^{2+}] [\text{OH}^-]^2 = 4[\text{Mg}^{2+}]^3 = 10^{-11},$$

$$\text{whence } [\text{Mg}^{2+}] = \sqrt[3]{2.50 \times 10^{-4}} = 1.36 \times 10^{-4} \text{ (gm.-ion/litre).}$$

$$\text{But } [\text{Mg}^{2+}] \text{ (gm.-ion/litre)} = \text{Mg}(\text{OH})_2 \text{ (G.F.W./litre).}$$

The solubility is therefore

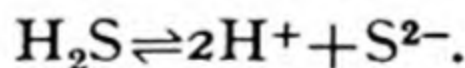
$$1.36 \times 58 \times 10^{-4} = \underline{0.0079 \text{ gm./litre.}}$$

Applications of Solubility Product. In qualitative analysis, most of the 'wet' tests depend upon the formation of a precipitate. In Group II, for instance, various metals are precipitated as their sulphides, while later in the tables calcium, strontium, and barium are precipitated as their carbonates. Similarly, chlorides are recognized by the formation of a precipitate of silver chloride, and sulphates by the precipitation of barium sulphate. In all these reactions, and their like, conditions are so arranged that the solubility products of the precipitated substances are momentarily exceeded.

The Precipitation of Sulphides. The solubility products of some common metallic sulphides are as follows:

HgS	10^{-52}	NiS	10^{-21}
CuS	10^{-41}	ZnS	10^{-20}
CdS	10^{-29}	FeS	10^{-19}
SnS	10^{-28}	MnS	10^{-16}

In aqueous solution hydrogen sulphide behaves as an extremely weak dibasic acid:



$$\frac{[\text{H}^+]^2 [\text{S}^{2-}]}{[\text{H}_2\text{S}]} = K_a = 10^{-21}.$$

In a solution of the gas saturated at normal temperature $[\text{H}_2\text{S}] = 0.1 \text{ M}$, hence for such a solution:

$$[\text{S}^{2-}] = \frac{10^{-22}}{[\text{H}^+]^2},$$

and in the presence of normal hydrochloric acid ($[\text{H}^+] = 1$):

$$[\text{S}^{2-}] = 10^{-22} \text{ gm.-ion per litre.}$$

The solubility product of stannous sulphide is 10^{-28} (see table). It follows that stannous sulphide will be precipitated, in the presence of normal hydrochloric acid, until the concentration of metal ion $[\text{Sn}^{2+}]$ is reduced to 10^{-6} gm.-ion per litre, for then $[\text{Sn}^{2+}][\text{S}^{2-}] = 10^{-6} \times 10^{-22} = 10^{-28}$. The residual concentration of the ions Cd^{2+} , Cu^{2+} , and Hg^{2+} will be much less, reaching in the case of Hg^{2+} the extreme of 10^{-30} gm.-ion per litre.

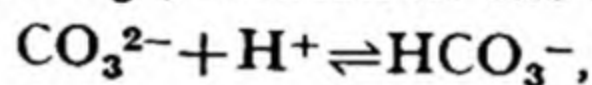
For the precipitation of nickel sulphide in the presence of normal hydrochloric acid the concentration of Ni^{2+} must be greater than 10 gm.-ion per litre, which is much greater than any employed in a properly conducted qualitative analysis. For the cations of the other metals in the second group of the above table the necessary concentration for precipitation as sulphide would much exceed that in saturated solutions of most of their salts.

The Precipitation of Hydroxides. The solubility products of some hydroxides are as follows:

$\text{Fe}(\text{OH})_3$	10^{-38}	$\text{Zn}(\text{OH})_2$	10^{-15}
$\text{Al}(\text{OH})_3$	10^{-38}	$\text{Mg}(\text{OH})_2$	10^{-11}
$\text{Cr}(\text{OH})_3$	10^{-30}	$\text{Ca}(\text{OH})_2$	10^{-5}

The hydroxides of the tervalent metals listed above are precipitated in qualitative analysis by using a solution containing both ammonia and ammonium chloride, i.e. a buffer mixture of base, NH_3 , and the conjugate cation acid, NH_4^+ (see p. 228). Here the great difference in the solubility products ensures that the metals in the second column are not precipitated (cf. example, p. 235).

The Solubility of 'Insoluble' Salts in Acid Solutions. We consider first the important example of the attack by water containing dissolved carbon dioxide on calcium carbonate. It was shown on p. 230 that $\text{p}K_b$ for carbonate ion is 3.8, whence it follows that $\text{p}K_a$ for its conjugate acid HCO_3^- , formed in the reaction



is $\text{p}K_a = 14 - \text{p}K_b = 10.2$ (see p. 220), and $K_a = 10^{-10.2} = 6.3 \times 10^{-11}$.

Therefore
$$\frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = 6.3 \times 10^{-11}$$

or
$$\frac{(\text{carbonate})}{(\text{bicarbonate})} = \frac{6.3 \times 10^{-11}}{[\text{H}^+]}$$

Hence the carbonate/bicarbonate ratio, fixed by the pH, is very small except in strongly alkaline solutions. When calcium carbonate is brought into contact with water through which a steady stream of normal air is passing, the pH will be 5.7 (p. 224), and carbonate initially dissolving is almost wholly converted into bicarbonate. The concentration $[\text{Ca}^{2+}]$ of calcium ion, present

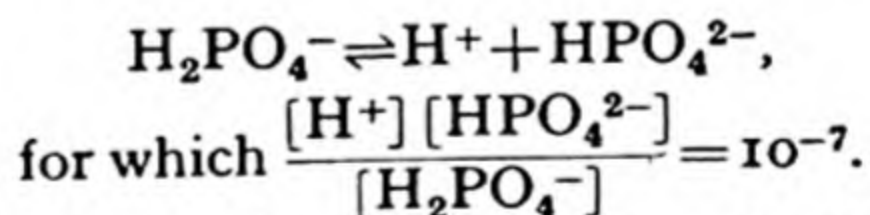
very largely as dissolved $\text{Ca}(\text{HCO}_3)_2$, increases, as does also the small carbonate concentration $[\text{CO}_3^{2-}]$, to a limit when the solubility product $[\text{Ca}^{2+}][\text{CO}_3^{2-}]$ reaches its constant value prescribed by the temperature. Equilibrium is simultaneously attained at that point between carbonate and bicarbonate, and between the solution and the solid: the amount of carbonate dissolved reaches the maximum for the conditions.

At 15° in one litre of water kept fully aerated 62.4 *milligrams* of CaCO_3 (as 98 *milligrams* of $\text{Ca}(\text{HCO}_3)_2$), and 1.4 *milligrams* of unchanged CaCO_3 are dissolved at saturation. When the water is kept saturated with pure carbon dioxide at 1 atmosphere pressure ($\text{pH}=3.95$) 1.08 *grams* of CaCO_3 (as 1.76 gm. of $\text{Ca}(\text{HCO}_3)_2$) and only 10^{-4} gm. of CaCO_3 as such are dissolved at saturation. The calculated solubility product $[\text{Ca}^{2+}][\text{CO}_3^{2-}]$ is 8.0×10^{-9} , so that if carbonate ion were not so strong a base but were instead a neutral ion (like nitrate, NO_3^-) the solubility of CaCO_3 (G.F.W.=100) would be independent of pH and amount to only $\sqrt{8.0 \times 10^{-9} \times 100} = 9$ *milligrams* per litre. This is also approximately the solubility in a strongly alkaline solvent such as aqueous ammonia.

Although orthophosphate ion PO_4^{3-} is a base even stronger than carbonate:

$$\frac{[\text{H}^+][\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]} = 10^{-12},$$

and calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, is therefore easily attacked by acid water, the calcium hydrogen phosphate produced, CaHPO_4 , is little more soluble than the original solid. Hence in discussing solubility we may assume the solid to be CaHPO_4 , yielding the easily soluble phosphate, $\text{Ca}(\text{H}_2\text{PO}_4)_2$. Here we are concerned with the equilibrium:

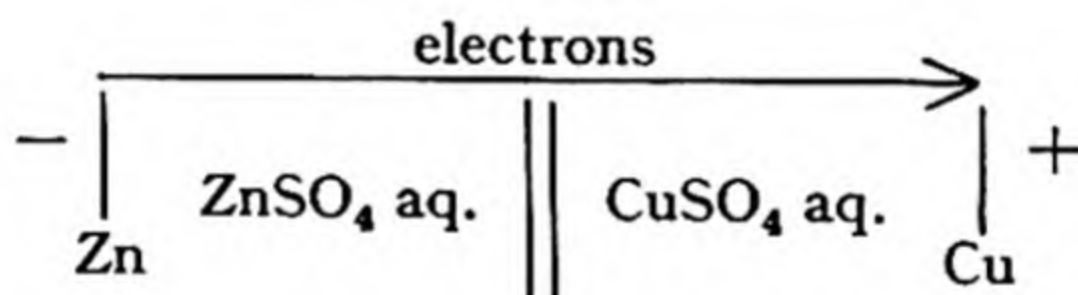


On comparing this expression with that controlling the solubility of calcium carbonate (see above) we see in this case a less favourable value of the equilibrium constant. This is, however, an advantage in the large-scale application of *phosphorite* ($\text{Ca}_3(\text{PO}_4)_2$) as a dressing for arable land. Water containing carbon dioxide releases a constant small concentration of soluble phosphate as $\text{Ca}(\text{H}_2\text{PO}_4)_2$, sufficient for healthy plant growth, over many seasons after the application, and very little phosphate is lost by leaching. On the contrary 'superphosphate,' containing the soluble calcium phosphate and made from phosphorite by treatment with sulphuric acid (p. 345), is wasteful, for all soluble phosphate is released quickly and mostly lost by leaching.

CHAPTER XVIII

ELECTROMOTIVE FORCE

Voltaic Cells. In this chapter we shall see how Volta's discovery (1800) of what is now called the voltaic cell (p. 102) has led to a final solution of the eighteenth-century problem of the 'affinities' of the metals (p. 73). The simplest voltaic cell consists of two 'half-cells' in each of which a metal electrode dips into an aqueous solution of one of its soluble salts. These half-cells, containing different metals, are joined by some means, for example a thin porous earthenware partition, which allows the passage of dissolved ions but prevents the bulk mixing of the salt solutions. We take as an example the *Daniell cell*, with electrodes of copper and zinc, dipping respectively into solutions of copper and zinc sulphate:



On joining the electrodes to the terminals of a galvanometer a current (of electrons) is proved to flow through it from the zinc to the copper electrode. The current is derived at the zinc electrode, or *negative pole*, from its dissolution in the reaction $\text{Zn} = \text{Zn}^{2+}_{\text{aq.}} + 2e$, and is carried away from the copper electrode, or *positive pole*, by the deposition of copper, in the converse reaction $\text{Cu}^{2+}_{\text{aq.}} + 2e = \text{Cu}$. In these electrochemical equations the symbol 'e' stands for a mole of electrons. The whole electrical circuit embraces three distinct modes of electrical transport: (a) *metallic* conduction, solely by electrons, in the external connections; (b) *electrolytic* conduction, by all the ions Cu^{2+} , Zn^{2+} , and SO_4^{2-} , in the solution between the electrodes; (c) at the interfaces between electrodes and solution metallic and electrolytic conduction are interchanged by the discharge or production of ions.

The flow of current is thus derived from the net chemical reaction

$\text{Zn} + \text{Cu}^{2+}_{\text{aq.}} = \text{Zn}^{2+}_{\text{aq.}} + \text{Cu}$, of which the components $\text{Zn} = \text{Zn}^{2+}_{\text{aq.}} + 2e$ and $\text{Cu}^{2+}_{\text{aq.}} + 2e = \text{Cu}$ take place separately at the negative and positive poles respectively. Since electricity flows between the electrodes there must be a difference of electric potential, or *electromotive force* (e.m.f.), between them. A *potentiometer* is an instrument for measuring such e.m.f. In its simplest form it consists of a long uniform wire stretched between two points of known difference of potential; with a fixed connection at one end of this wire and a second, sliding, contact any potential difference, or e.m.f., can be tapped off up to the maximum between the ends of the wire. We connect the Daniell cell through a galvanometer to the potentiometer so that the e.m.f. in the wire opposes that of the cell. On now gradually moving the sliding contact the current registered on the galvanometer decreases, becomes zero, and is then reversed. The greater e.m.f. from the potentiometer is then forcing a reversal of the original chemical reaction in the cell: copper is dissolving to $\text{Cu}^{2+}_{\text{aq.}}$ at what has become the *anode*, while zinc is deposited on the *cathode*. At the point of exact balance (and zero current), giving the e.m.f. E of the Daniell cell, clearly there is a corresponding balance or equilibrium between the solutions and the electrodes in contact with them, each losing and gaining electrons at equal rates. Since this condition of equilibrium is associated with no current flow it must be the normal state of the electrodes when the cell is on 'open circuit' (p. 242). For the Daniell cell containing saturated solutions of the salts $E_{15^\circ} = 1.093$ volt.

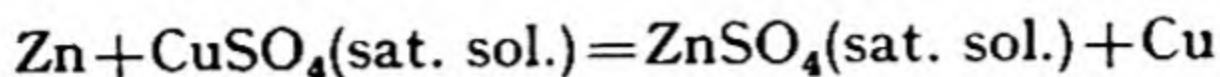
By definition one joule of work can be obtained from one coulomb of electricity flowing between points differing in potential by one volt. Since $2 \times 96,500$ coulombs (the charge upon 2 moles of electrons, or 2 faradays) must flow between electrodes differing in potential by 1.093 volt for every gm.-atom of zinc dissolved, the corresponding work obtainable is

$$W_{15^\circ} = 1.093 \times 96,500 \times 2 = 210,900 = 210.9 \text{ kilojoules}$$

$$\equiv \frac{210.9}{4.184} = 50.4 \text{ kcal.}$$

By mixing powdered zinc with aqueous copper sulphate in a calorimeter the heat of reaction ΔH per gram-atom of zinc is found to be -55.2 kcal. Hence by carrying out the reaction electrochemically it is possible to obtain nearly all the chemical energy in the form of useful work. From the way in which the e.m.f. is measured on the potentiometer it is evidently the *maximum* e.m.f. possible for the cell, and the calculated work is the maximum obtainable from the cell reaction. As explained in Chapter XI, p. 123, the maximum

work is equal to the decrease of free energy ΔG . Hence for the reaction



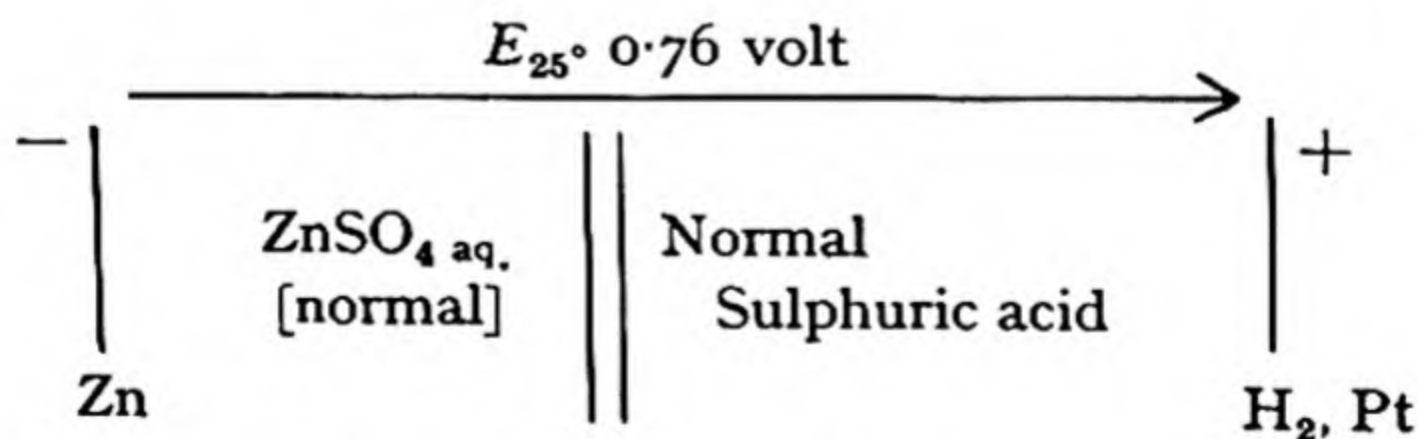
we are able to evaluate all the energy terms connected by the equation

$$\Delta G = \Delta H - T\Delta S : \Delta G = -50.4 \text{ kcal.} \quad \Delta H = -55.2 \text{ kcal.}$$

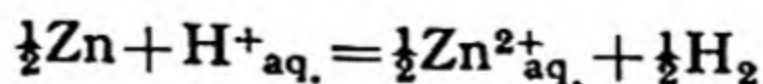
$$T\Delta S = -4.8 \text{ kcal.}$$

The Hydrogen Electrode. We have seen in the last section that, depending on the conditions, at the interface between a metal, e.g. Zn or Cu, and a solution of one of its soluble salts either the reaction $\text{M} = \text{M}^{2+}_{\text{aq.}} + 2e$ or its reverse can take place, or on open circuit the equilibrium $\text{M} \rightleftharpoons \text{M}^{2+}_{\text{aq.}} + 2e$ be established. The hydrogen electrode provides a means by which the reaction $\text{H}_2 = 2\text{H}^{+}_{\text{aq.}} + 2e$ or its reverse can proceed, or the corresponding equilibrium be set up, when the electrode is in contact with a solution containing hydrogen ions. A thin plate of platinum, with a wire of the same metal welded to it for external connections, is 'platinized,' that is coated by electrolysis with a deposit of 'platinum black,' which is simply the very finely divided metal. The electrode so prepared is mounted in a glass tube and immersed in an acid solution. By passing a slow stream of pure hydrogen through the tube it can be arranged that the electrode is successively exposed to a bubble of gas or to the solution. It is hardly surprising that a catalyst, here platinum black, should be necessary to cause the electrode reaction $\text{H}_2 = 2\text{H}^{+}_{\text{aq.}} + 2e$ to take place sufficiently rapidly (see further, p. 249).

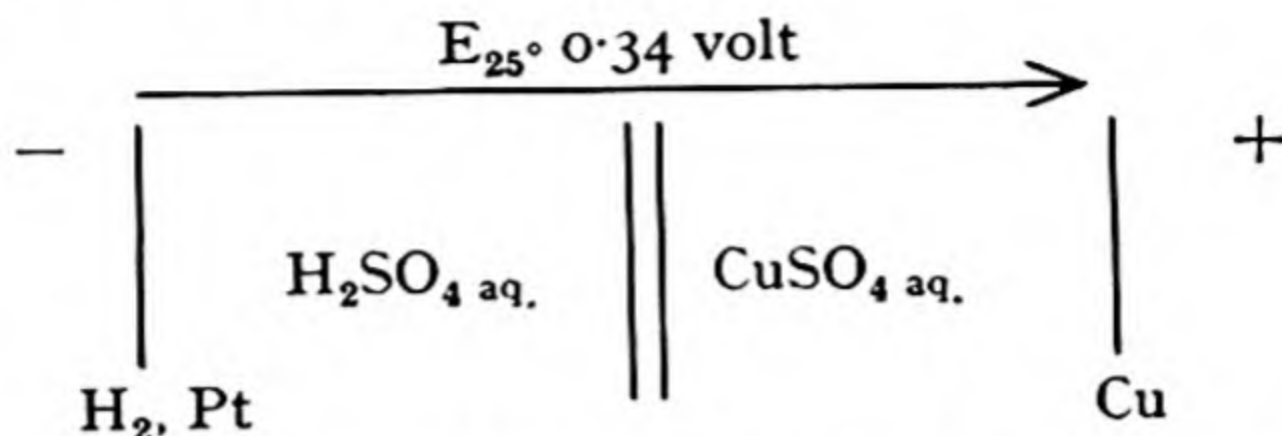
The Hydrogen Electrode in Voltaic Cells.



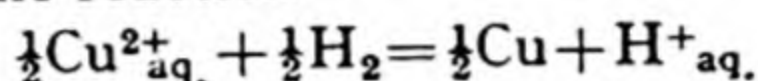
In the cell shown in the diagram the hydrogen electrode replaces that of copper in the Daniell cell. The e.m.f. measured at 25° is 0.76 volt, with zinc again as the negative pole. The free energy of the reaction



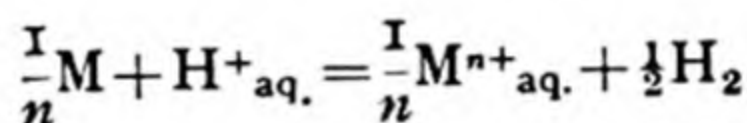
is therefore $-0.76 \times F$ (joules) where F is one faraday. If the Zn half-cell is exchanged for that of copper:



we find that the hydrogen electrode becomes the *negative* pole, and the free energy of the reaction



is $-0.34 \times F$ (joules). For the reverse reaction the free energy is hence $+0.34 \times F$ (joules). From the above examples it should be clear how in principle the free energy of reactions expressed in general as



can be ascertained for any metal M. Special methods have been devised for metals such as those of Groups I and II which attack water.

Electrode Potentials. In our previous discussion we have not been obliged to form any detailed conception of the nature of the equilibrium at the interface electrode-salt solution in a voltaic cell on open circuit or when its e.m.f. is balanced on a potentiometer. If we suppose that the whole potential difference expressed by the measured e.m.f. is composed of contributory differences at each electrode, we are led to picture interface conditions such as are shown in Fig. 49 for the Daniell cell. At a given temperature, and

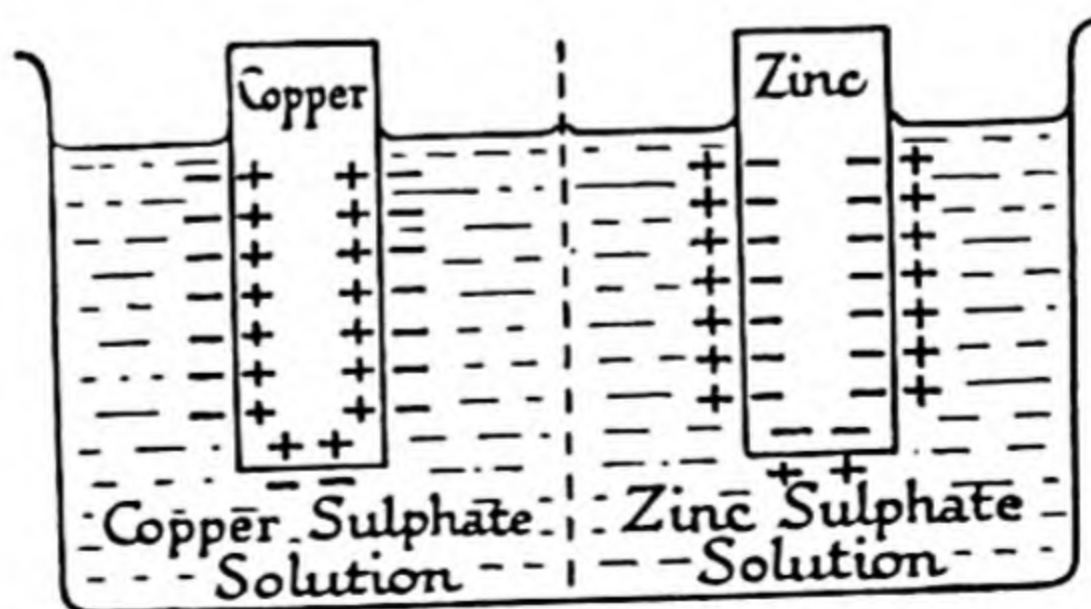
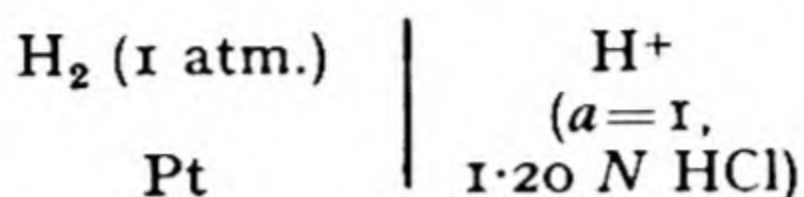
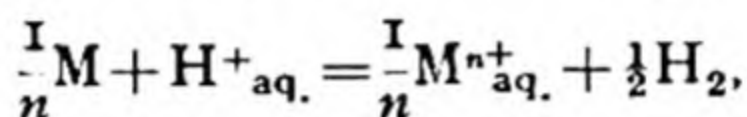


FIG. 49

for salt solutions of definite concentrations (say 'normal'), each electrode interface is seen as the seat of a specific potential difference. There is, however, no known method by which such *single* potential differences can be determined. A convenient *relative* measure may nevertheless be set up by arbitrarily assigning the value zero to the potential difference at a standardized hydrogen electrode (for meaning of activity a , see p. 200).

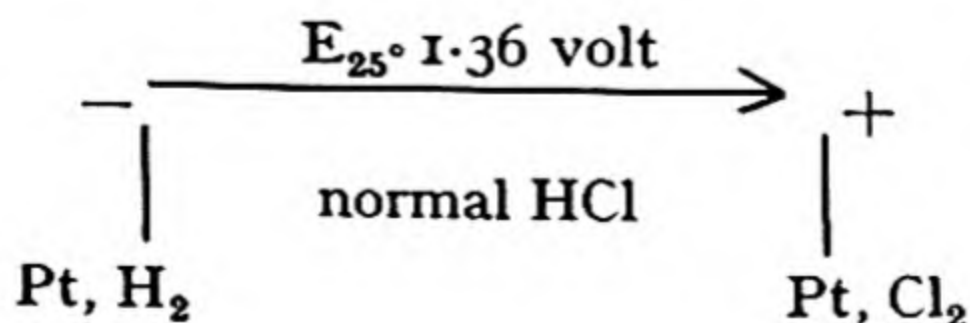


The Electrochemical Series of the Metals. In the cells formed by combining suitable electrodes of the majority of the commoner metals with the hydrogen electrode specified above, the metal is the *negative* pole, i.e. the cell reaction is of the type

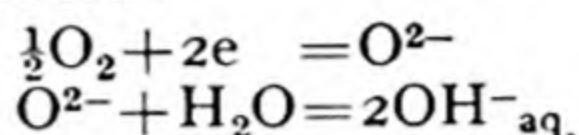


with discharge of hydrogen ions. On the *hydrogen scale* as defined above the e.m.f. of such a cell is equal to the electrode potential E_M of the metal M , and the free energy of the cell reaction is $-E_M \times F$ (joules). In similar cells formed with electrodes of a limited number of common metals, such as *copper*, *silver*, and *mercury*, the metal electrode is the *positive* pole, at which metallic ions are discharged. For these metals the free energy of a reaction *in the direction shown above* is $+E_M \times F$ (joules), because the (spontaneous) cell reaction is in the reverse direction (cf. copper, p. 242). Hence in the list of electrode potentials given below each potential for a metal is given the sign such that when the potential is multiplied by F , it correctly gives the free energy of reaction between metal and hydrogen ion. It is easily remembered that when in combination with the hydrogen electrode the metal is the *negative* pole, its electrode potential takes the *negative* sign, and conversely.

Electrode Potentials of Non-metals. Halogen electrodes, operating similarly to the hydrogen electrode, have been successfully constructed and combined with the latter in voltaic cells, such as that shown diagrammatically below:



The cell reaction, $\text{H}_2 + \text{Cl}_2 = 2\text{H}^+_{\text{aq.}} + 2\text{Cl}^-_{\text{aq.}}$ requires the formation of ions at *both* electrodes, that of the halogen being the positive pole. Hence, extending to non-metals the rule adopted for metal electrode potentials, we reckon halogen potentials *positive*. Gaseous oxygen electrodes are not satisfactory: the potential corresponding to the successive electrode reactions



is calculated indirectly.

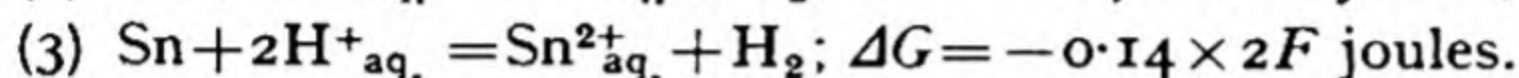
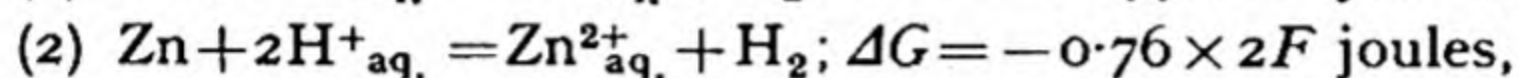
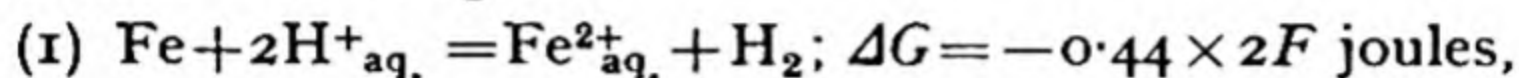
ELECTROCHEMICAL SERIES (25°)

<i>Element</i>	<i>Ion</i>	<i>Electrode Potential in Volts</i>	<i>Element</i>	<i>Ion</i>	<i>Electrode Potential in Volts</i>
Lithium	Li^+	-3.02	Lead	Pb^{2+}	-0.12
Rubidium	Rb^+	-2.92	Hydrogen	H^+	0.00
Potassium	K^+	-2.92	Copper	Cu^{2+}	+0.34
Barium	Ba^{2+}	-2.90	Mercury	Hg_2^{2+}	+0.80
Sodium	Na^+	-2.71	Silver	Ag^+	+0.80
Magnesium	Mg^{2+}	-2.34	Gold	Au^+	+1.68
Aluminium	Al^{3+}	-1.66			
Manganese	Mn^{2+}	-1.10	Oxygen	OH^-	+0.41
Zinc	Zn^{2+}	-0.76	Iodine	I^-	+0.53
Iron	Fe^{2+}	-0.44	Bromine	Br^-	+1.07
Cadmium	Cd^{2+}	-0.40	Chlorine	Cl^-	+1.36
Cobalt	Co^{2+}	-0.29	Fluorine	F^-	+2.85
Nickel	Ni^{2+}	-0.23			
Tin	Sn^{2+}	-0.14			

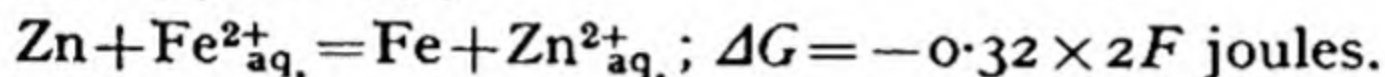
The Electrochemical Series. The electrode potentials listed are strictly accurate for solutions in which the relevant ion has unit activity, but they may be used as good approximations over a considerable range of activities and corresponding concentrations. For an ion with positive charge n^+ the potential becomes more *negative* by $0.059/n$ volt for a decrease of activity by one power of ten, e.g. from 1.0 to 0.1. Hydrochloric acid of normality 1.2 contains hydrogen ion at unit activity, and acid 0.13 normal contains the ion at activity 0.1 (see p. 200). The series is of great assistance in explaining the general chemical properties of metals, so that, while there is no need to learn the numerical values of the electrode potentials, the relative positions occupied in the series by the commoner metals may usefully be memorized. Some of the chief applications of the series will be considered here.

(i) *Chemical properties.* The position of a metal in the electro-

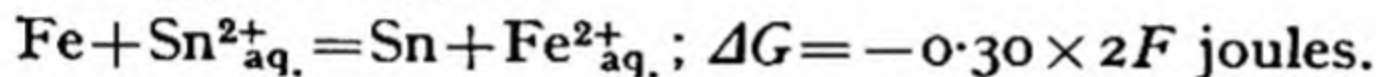
chemical series is a rough indication of its chemical activity. Metals high in the series are very reactive; they include the alkali-metals, Li, Na, K, Rb, and Cs, and the alkaline-earth metals, Ca, Sr, Ba. Further down the list come the less reactive metals such as Co, Ni, Sn, and Pb; while those below hydrogen are comparatively unreactive, some of them being so resistant to most reagents as to have earned the title of 'noble.' Any metal in the series will displace from solutions of appropriate salts any metal below it; conversely, it is itself displaced by a metal above it. To verify this principle consider the three metals iron, zinc, and tin. We write down the cell reactions on which the electrode potentials are based, and their free energies:



Subtract (1) from (2):



Subtract (3) from (1):



We see that displacement of iron by zinc, and of tin by iron, are spontaneous reactions, since they are accompanied by decrease of free energy. It will be obvious that no metal below hydrogen in the list will normally displace hydrogen from a dilute acid, and that, of the metals above hydrogen, those will react most vigorously which are furthest removed.

An interesting example of the use of the electrochemical series is in the explanation of the relative rates of corrosion of galvanized iron (iron covered with zinc) and tin-plate (iron covered with tin). Everybody knows that a 'tin' made of tin-plate will rust very quickly once the tin covering has been perforated by a scratch or cut, while a galvanized iron dust-bin will stand up to years of violent treatment by the emissaries of the Sanitary Authority without rusting. The explanation is very simple. Suppose that a piece of galvanized iron has had the zinc scraped off in a certain spot, and that the article is then exposed to air and rain. The rain-water is slightly acid, having absorbed carbon dioxide from the air; hence the electrolytic cell *zinc | dilute acid | iron* is set up, and as the above calculations show, it is the zinc and not the iron which passes into solution. But the rusting of iron depends primarily upon the formation of ferrous ions (p. 590), and since these are not formed, the iron does not rust. The zinc coating, on the other hand, is slowly destroyed. Under similar conditions, tin-plate forms the

cell *tin* | *dilute acid* | *iron*. Here, the iron passes into solution as ferrous ions, and rusting (formation of hydrated ferric oxide) rapidly takes place.

(ii) *Attack of water upon metals: passivity.* The concentration (or activity) of hydrogen ion in pure water (free from dissolved carbon dioxide) is close to 10^{-7} gm.-ion per litre at ordinary temperature (p. 216). Hence by the rule given on p. 244 the potential of a hydrogen electrode immersed in pure water should be $-0.059 \times 7 = -0.41$ volt. It follows that no metals below iron in the series are attacked or corroded by water. If allowance is made for over-voltage in the discharge of hydrogen (p. 249) iron should also be immune from attack by pure water, as experiment has proved (p. 590). We should, however, expect all metals in the series above and including zinc to react with pure water with a vigour increasing as the series is ascended. The common metals, zinc, aluminium, and magnesium, on the contrary, owe their principal uses to resistance to such attack, and it is not until sodium is reached that such a prediction is verified.

When a freshly abraded surface of any of the three metals is exposed to air a very thin, invisible, but perfectly adherent film of oxide forms on the surface almost instantaneously, and completely immunizes the metal from further attack by oxygen, or water, at ordinary temperature. Aluminium is violently dissolved by concentrated hydrochloric acid or by water containing alkali, both of which reagents dissolve the film: but the metal may be immersed without apparent action in concentrated nitric acid, in which the film is preserved. An experiment, known to the facetious as 'grandfather's whiskers,' dramatically demonstrates the vigour with which 'bare' aluminium is attacked by water. A few drops of aqueous mercuric chloride are spread over the surface of a piece of aluminium foil by the use of a glass rod, which, by scratching, locally impairs the film and exposes the metal. Mercury is deposited (as the electrochemical series predicts) and forms with the aluminium an amalgam on which a protective oxide film cannot be developed. Long white 'whiskers' of aluminium oxide rapidly extend from the surface of the foil, which becomes so heated by the vigour of the action that it cannot be held in the hand.

When protected by such means a metal is said to be in a 'passive' state, and the phenomenon is termed 'passivity.' A sheet of iron is readily rendered passive by immersion in concentrated nitric or chromic acid, and in this state is quite inert when dipped into aqueous copper nitrate; but a slight tap on its surface breaks the continuity of the film and a deposit of copper immediately follows. On passive iron the presence of a film has been directly proved by dissolving the underlying metal in aqueous iodine, when the very

thin and transparent film remains for inspection. It is one of the major misfortunes of nature that a protective film is *not* formed upon iron by contact with air, with the result that a considerable portion of the world's wealth is annually spent on paint and other protective agencies.

Protective films are, however, formed spontaneously in air upon some iron alloys, notably one containing 15–20 per cent of chromium which, as 'stainless steel,' has come into widespread use. It owes its properties to a permanent passivity; after damage by mechanical wear the film is spontaneously restored by air oxidation. Pure chromium, now so widely seen in electroplating, is also continuously passive. The mirror lustre of chromium plate and 'stainless' steel shows that the film is sufficiently thin to exert no appreciable effect on the reflection of light from the metal surface. It is obvious that the higher the degree of protection a film can give, the thinner it must be.

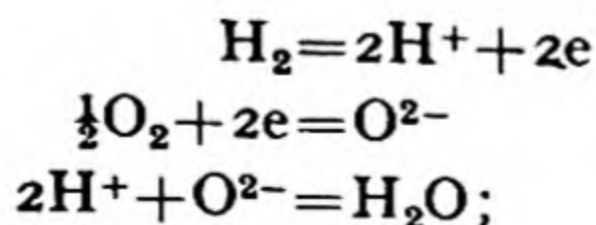
(iii) Further general correlations between the electrochemical series and general chemical properties are set out on p. 248.

Decomposition Voltage—'Nascent' Hydrogen. If the cell containing normal hydrochloric acid shown on p. 243 above is connected to a potentiometer its e.m.f. will be just balanced at 1.36 volt, when no current flows through the cell. When the potentiometer contact is moved to a point corresponding to a larger opposing e.m.f. the cell reaction will be reversed, i.e. normal hydrochloric acid will be electrolysed, and hydrogen and chlorine released at the electrodes. This example shows that the e.m.f. of such a cell may be alternatively viewed as the *decomposition voltage* of the electrolyte contained in it. In an electrolytic cell containing normal hydrochloric acid and furnished with platinized platinum electrodes steady electrolysis will not start until the voltage between the electrodes exceeds 1.36 volt.

The free energy of formation from its elements of hydrochloric acid in normal aqueous solution— $\frac{1}{2}\text{H}_2 + \frac{1}{2}\text{Cl}_2 = \text{HCl}$ (N solution)—is:

$$\frac{(1.36 \times 96.5)}{4.18} = 31.4 \text{ kcal. (cf. p. 240).}$$

Conversely, when the free energy of formation is known from other sources the decomposition voltage may be calculated. The free energy of formation of water— $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) = \text{H}_2\text{O}(\text{l})$ —is -56.7 kcal. From an electrochemical standpoint the reaction consists of the stages:



<i>Metal</i>	<i>Electrode Potential in Volts</i>	<i>With Water or Steam</i>	<i>With Common Acids</i>	<i>With Air</i>	<i>Further General Properties</i>
Potassium	-2.92	Liberate hydrogen in the cold	Can liberate hydrogen from suitable dilute acids	Oxidized extremely readily	Oxides combine with water to form hydroxides; the latter are strong bases soluble in water.
Sodium	-2.71				
Barium	-2.90				
Calcium	-2.87				
Magnesium	-2.34	Liberate hydrogen at red heat	Do not liberate hydrogen, but are attacked by nitric acid	Burn if heated in air or oxygen	No metal above aluminium can form part of an anion; aluminium and metals below it often do so. Carbonates of all metals below sodium are insoluble in water.
Aluminium	-1.66				
Zinc	-0.76				
Iron (Fe^{2+})	-0.44				
Cadmium	-0.40	No action below white heat	No action	Form the oxide on heating, but without ignition	Hydroxides insoluble in water, and much less basic than those of K, Na, Ba, and Ca. Oxides stable to heat and insoluble in water. Metals lower than aluminium can be deposited electrolytically from aqueous solutions of their salts. The lower the position in the table, the greater is the tendency shown by the metals to form complex compounds rather than simple ionic ones. The general stability of the metallic compounds decreases as the list is descended.
Cobalt	-0.29				
Nickel	-0.23				
Tin	-0.14				
Lead	-0.12	No action	No action	No action	
[HYDROGEN	0.00]				
Copper (Cu^{2+})	+0.34				
Mercury (Hg_2^{2+})	+0.80				
Silver	+0.80	No action	No action	No action	
Gold	+1.68				

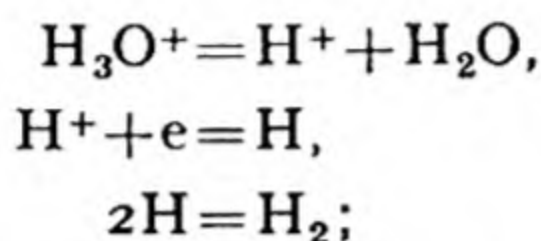
(See p. 247)

hence the decomposition voltage of water should be

$$\frac{(56.7 \times 4.18)}{2 \times 96.5} = 1.23 \text{ volt.}$$

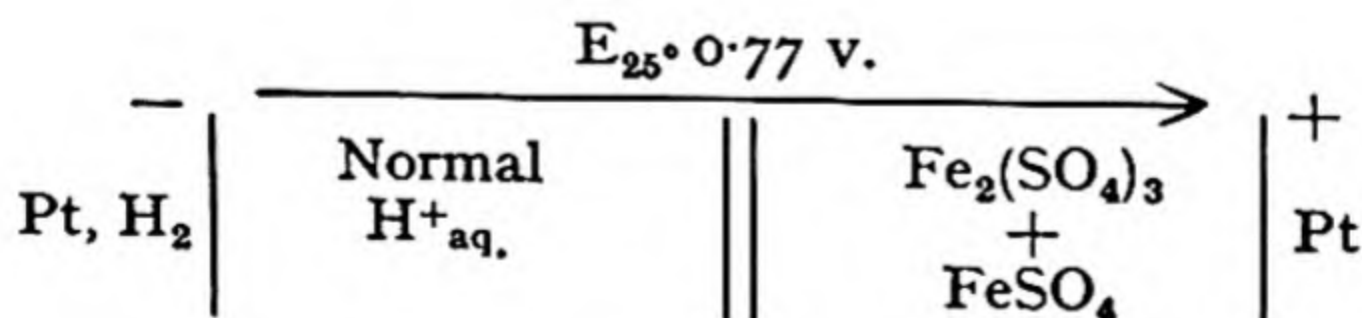
When the electrolysis of water (acidified with sulphuric acid) is conducted with platinized platinum electrodes the production of the gases at the electrodes starts from this voltage, but if the electrodes are formed of any other materials a higher voltage is found necessary to initiate electrolysis. The excess voltage over the theoretical (1.23 volt) is termed the *overvoltage*.

The discharge of a gas such as hydrogen at an electrode must proceed in stages:

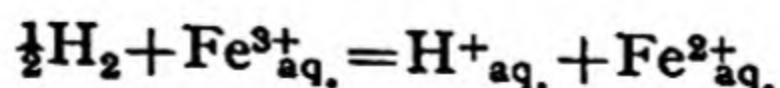


and if one or more of these stages occurs slowly discharge is impeded and a higher potential at the electrode will be required to maintain it. It is probably the last stage, $2\text{H}=\text{H}_2$, that is sluggish on most metals serving as electrodes, because the active atomic hydrogen becomes bonded to surface metal atoms. The largest hydrogen overvoltages are found at *mercury*, *zinc*, or *lead* cathodes. In the electrolysis of brine with a mercury cathode, as in the Castner-Kellner industrial process (p. 290), the hydrogen overvoltage is so high that sodium ion is more easily discharged than hydrogen ion. When zinc dissolves in acids the discharge of hydrogen ions passes through the stages given above, and the accumulation of hydrogen atoms on the zinc surface confers the strong reducing power formerly attributed to 'nascent' hydrogen.

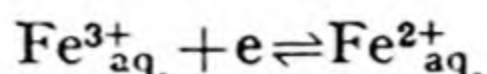
Further Types of Electrode. Electrochemical interactions between elements and their ions are not the only ways in which an electrode may gain or lose electrons. Consider the cell:



The measured e.m.f. at 25° , when $[\text{Fe}^{3+}] = [\text{Fe}^{2+}]$, is 0.77 volt, with the hydrogen electrode as the negative pole. The cell reaction is evidently



On open circuit the electrochemical equilibrium



exists at the positive pole. The platinum electrode at that pole serves as a carrier of electrons incoming from the negative pole, but is otherwise inert.

Oxidation-reduction Reactions. From the electrochemical standpoint *oxidation* is a process involving *removal* of electrons, and *reduction* the converse process. It is clear that oxidation and reduction must occur simultaneously, e.g. in the reaction in the preceding section hydrogen is oxidized to H^+ and ferric ion Fe^{3+} is reduced to ferrous ion Fe^{2+} ; it is therefore logical to employ the term *redox reactions*. Recalling the convention in regard to evaluating electrode potential (p. 242) we can say that 0.77 volt is the electrode potential of the *redox system* $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+} + e$. It may be noted that since the equilibrium $\text{metal} \rightleftharpoons \text{metal-cation} + ne$ is also a redox system the electrode potentials in the metallic series can be assimilated into a general series of oxidation-reduction potentials; the same applies to non-metal equilibria such as $\text{Cl}^- \rightleftharpoons \frac{1}{2}\text{Cl}_2 + e$.

In this generalized list of electrode potentials the redox systems are uniformly symbolized as *reduced form/oxidized form* or R/O:

GENERAL ELECTROCHEMICAL SERIES

R/O	Volts (25°)	R/O	Volts (25°)
Li/Li ⁺	-3.02	Sn ²⁺ /Sn ⁴⁺	0.15
Na/Na ⁺	-2.71	Fe(CN) ⁴⁻ /Fe(CN) ³⁻	0.36
Al/Al ³⁺	-1.66	I ⁻ / $\frac{1}{2}$ I ₂	0.53
Zn/Zn ²⁺	-0.76	Fe ²⁺ /Fe ³⁺	0.77
Cr ²⁺ /Cr ³⁺	-0.41	Br ⁻ / $\frac{1}{2}$ Br ₂	1.07
$\frac{1}{2}$ H ₂ /H ⁺	0.00	Cl ⁻ / $\frac{1}{2}$ Cl ₂	1.36
		F ⁻ / $\frac{1}{2}$ F ₂	2.85

The definite potentials listed reflect definite conditions for the redox systems, as follows:

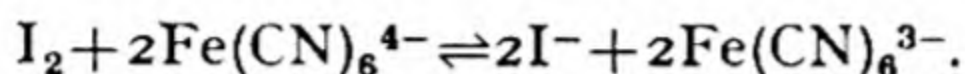
(a) When the system involves only one ionic species, e.g. metal-cation or halogen-anion, the solution contains 1 gm.-ion per litre.

(b) For systems involving two ionic species each is present in a concentration of 1 gm.-ion per litre: the ratio $[\text{R}]/[\text{O}]$ is therefore unity. A given system, *under these conditions*, reduces all systems beneath it in the list, and oxidizes all systems above it. Reducing power increases to a maximum upwards, and oxidizing power to a maximum downwards.

Effect of Change of Concentration. (1) Increase of [R] relative to [O] increases reducing power, and *raises* the position of the system in the list.

(2) Increase of [O] relative to [R] conversely increases power of oxidation, and *lowers* the position of the system.

Under normal conditions the ferrocyanide/ferricyanide system reduces the iodine system $I^-/\frac{1}{2}I_2$, but since the respective potentials do not widely differ the reaction is incomplete and equilibrium is reached when concentration changes consequent on the reaction have equalized the potentials:

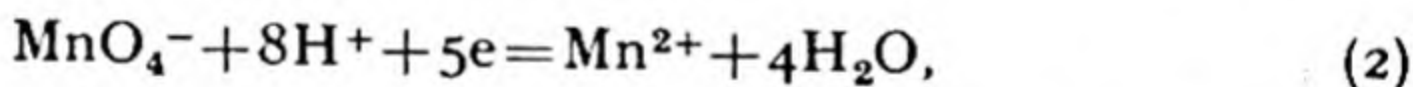


The reaction can be made complete in the direction right to left by adding zinc sulphate, when insoluble zinc ferrocyanide is precipitated, and [R] very drastically decreased. Hence ferricyanide may be quantitatively determined by titrating the iodine released in the presence of zinc sulphate.

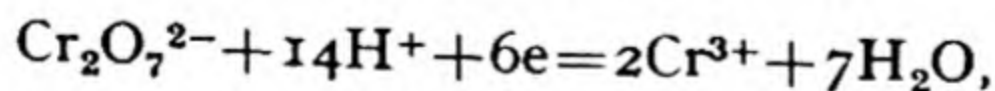
Some Redox Potentials not Directly Accessible. It is unfortunate that the electrochemical behaviour of the important oxidizing agents permanganate and dichromate cannot be directly studied. By a reducing agent, supplying electrons, such as oxalate anions:



the permanganate anion MnO_4^- , in the presence of acid, is reduced according to the electrochemical reaction:



which forms the basis of the use of permanganate in volumetric analysis. It is, however, not possible, by merely withdrawing electrons from aqueous manganous ion Mn^{2+} , to reverse the reaction. Therefore reaction (2) cannot give rise to a true electrode equilibrium. It is nevertheless possible to calculate approximately the free energy of reaction (2) when the electrons are supplied by the change $\frac{1}{2}H_2 = H^+ + e$, and so obtain an approximate estimate of the inaccessible electrode potential as 1.45–1.55 volt. Similar difficulties arise with the dichromate reaction:

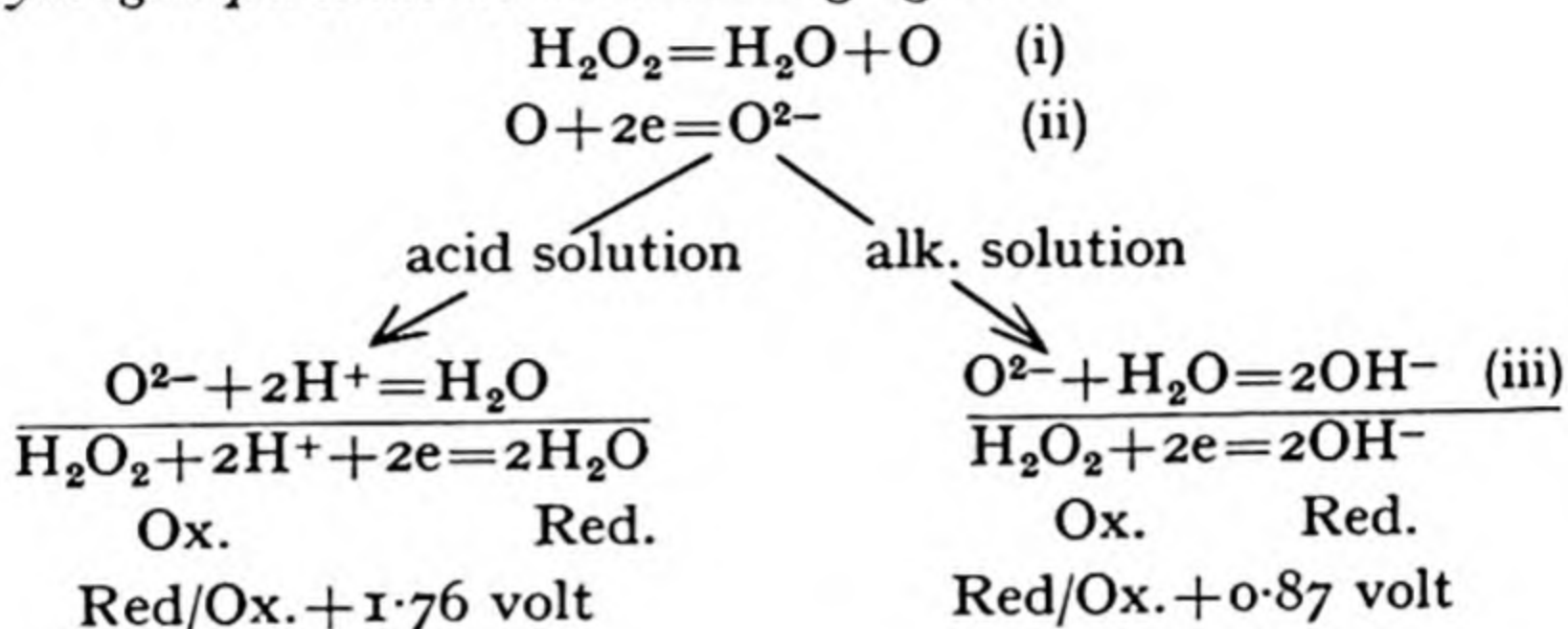


the electrode potential of which can be indirectly estimated as 1.30–1.40 volt. We may deduce that while permanganate oxidizes all the halogen anions Cl^- , Br^- , I^- , dichromate fails to oxidize Cl^- .

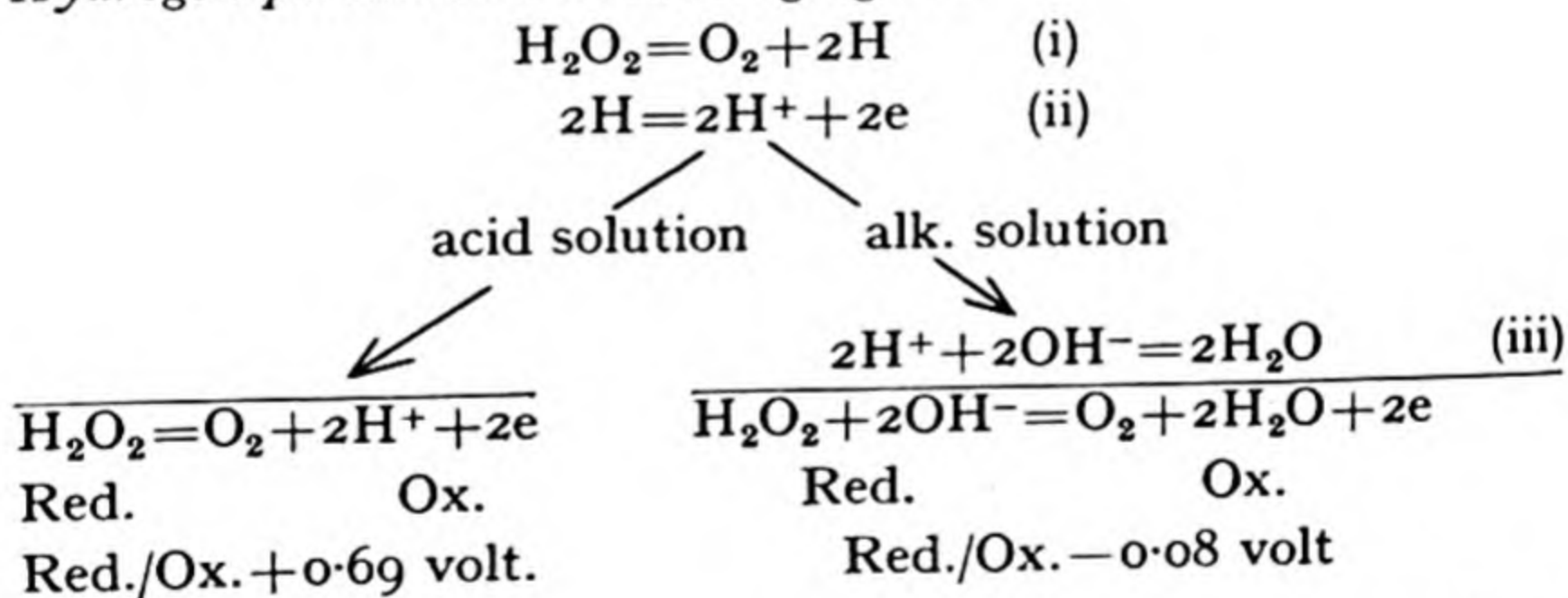
Application of Redox Potentials. Hydrogen peroxide, H_2O_2 , belongs to the small class of compounds (which includes also nitrite,

NO_2^- , p. 446) showing both oxidizing and reducing powers of comparable magnitudes (p. 508). This dual capacity originates from the close relation of the peroxide, itself only moderately stable, to two very stable molecules, water, and molecular oxygen, O_2 ; hydrogen peroxide may be considered as oxidized water $(\text{H}_2\text{O})\text{O}$, or as reduced oxygen, $\text{H}_2(\text{O}_2)$.

Hydrogen peroxide as an oxidizing agent:

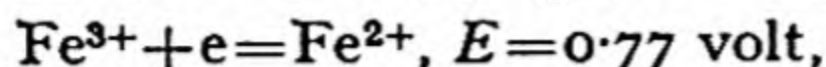
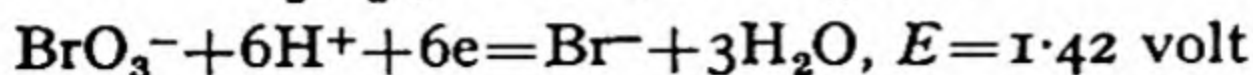
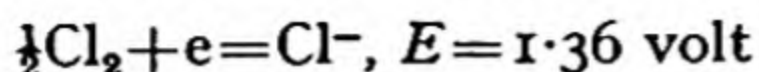


Hydrogen peroxide as a reducing agent:



Thus hydrogen peroxide exerts its greatest oxidizing power in acid solution (+1.76 volt), in which it can oxidize all the systems except that of fluorine in the table on p. 250; in particular ferrocyanide is oxidized to ferricyanide. Its most powerful reducing action requires alkaline solution (−0.08 volt), and it can reduce all systems below hydrogen in the table which are not changed chemically in alkaline solution, for example ferricyanide is reduced to ferrocyanide. The action of hydrogen peroxide on this system is thus reversed by changing the pH from low to high values. Systems with redox potentials more positive than 0.69 volt, for example permanganate (about +1.5 volt), are reduced by the peroxide even in acid solution.

Oxidation Number. From the electrochemical equations:



we see that chlorine and bromate (in acid solution) oxidize ferrous ions with about the same *power*, since their redox potentials stand in the redox series below that of the iron system by about the same amount. However, the bromate system has six times the oxidation *capacity* of the chlorine system; in practical chemistry oxidation capacity has no less importance than oxidizing power. The device of *oxidation number* (or *charge number*) simplifies the assessment of oxidation capacity.

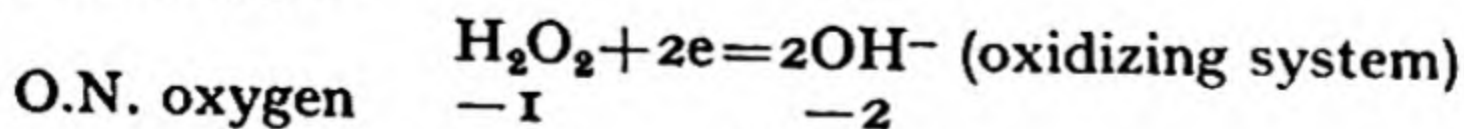
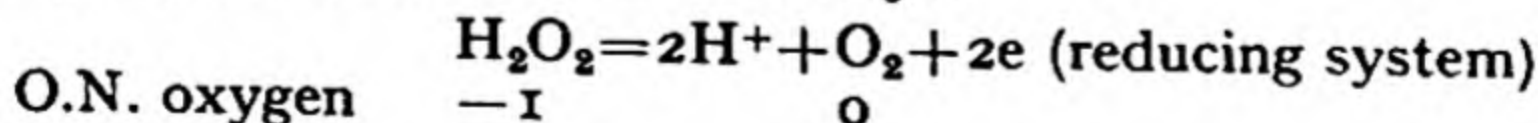
The oxidation number (O.N.) of an element as a simple monatomic ion is the same in sign and magnitude as the ionic charge:

	H^+	H^- (as in LiH)	Cl^-	O^{2-}	Fe^{2+}	Fe^{3+}
O.N.	+1	-1	-1	-2	+2	+3

Zero oxidation number is assigned to all atoms in their elementary forms— H_2 , O_2 , Cl_2 , Fe (metal), etc. In ascribing oxidation numbers to elements in compounds or compound ions a completely ionic constitution is arbitrarily assumed:

	ICl $\text{I}^+.\text{Cl}^-$	ICl_3 $\text{I}^{3+}.\text{(Cl}^-\text{)}_3$	I_2O_5 $(\text{I}^{5+})_2.\text{(O}^{2-}\text{)}_5$	IO_3^- $(\text{I}^{5+}).\text{(O}^{2-}\text{)}_3$
O.N. iodine	+1	+3	+5	+5
		MnO_4^- $\text{Mn}^{7+}.\text{(O}^{2-}\text{)}_4$	$\text{Cr}_2\text{O}_7^{2-}$ $(\text{Cr}^{6+})_2.\text{(O}^{2-}\text{)}_7$	
O.N. metal		+7	+6	
	H_2O $(\text{H}^+)_2.\text{O}^{2-}$	H_2O_2 $(\text{H}^+)_2.\text{(O}^-\text{)}_2$	F_2O $(\text{F}^-)_2.\text{O}^{2+}$	
O.N. oxygen	-2	-1	+2	

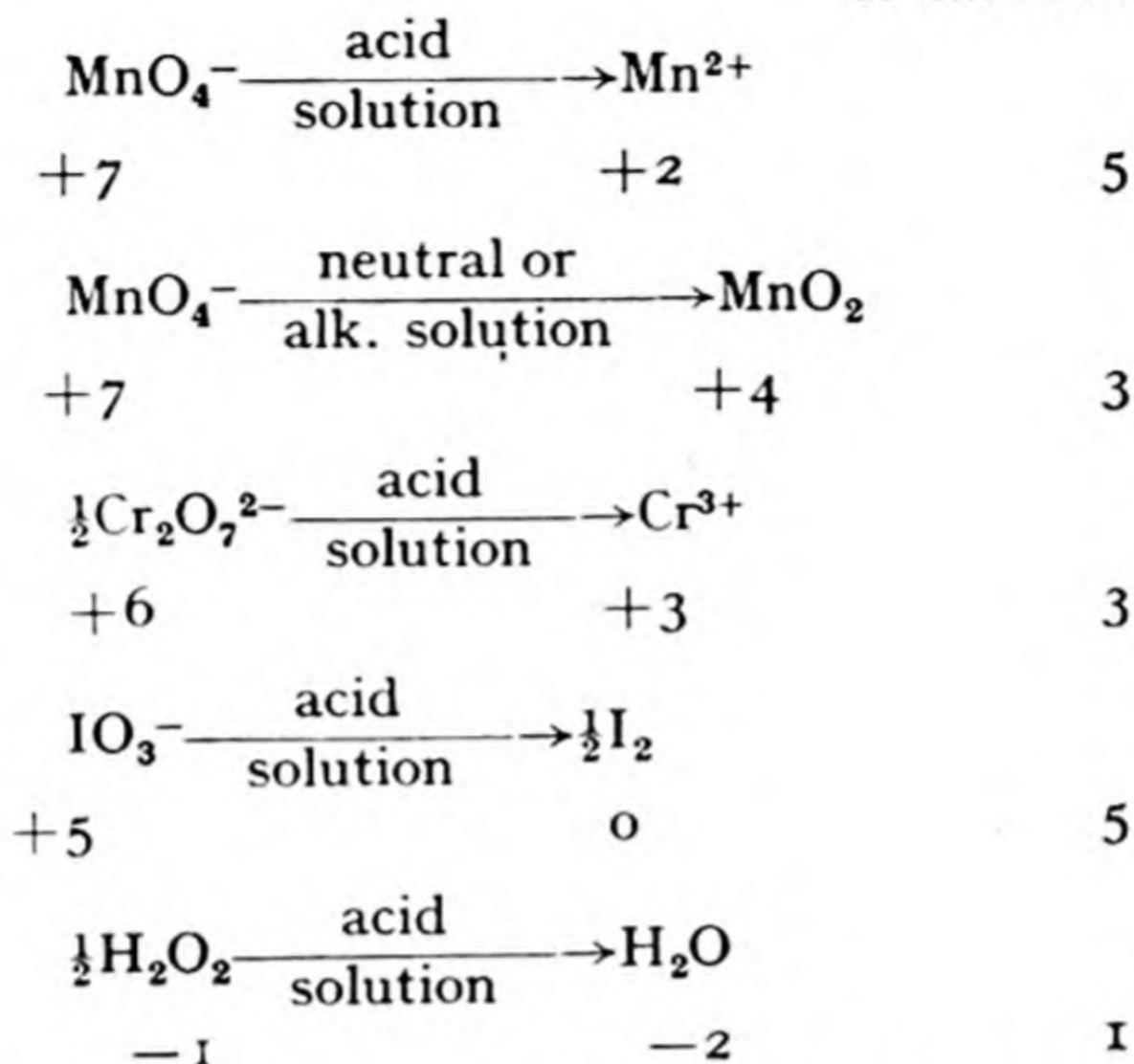
Hydrogen peroxide reacts in two ways:



(followed in acid solution by
 $2\text{OH}^- + 2\text{H}^+ = 2\text{H}_2\text{O}$)

Applications. The usefulness of oxidation numbers in assessing oxidation capacity will be understood from some examples:

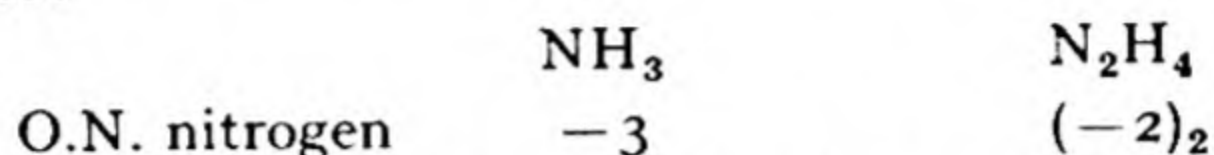
Decrease of O.N.,
or *oxidation capacity*



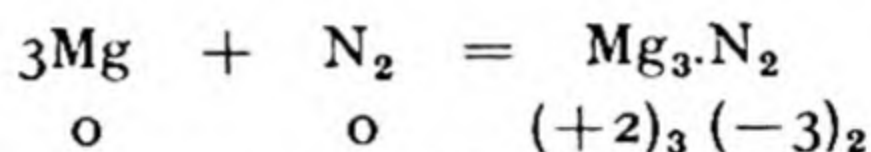
Stoichiometrical Calculations. For the purposes of calculating the results following from volumetric titrations the necessary stoichiometrical relations are now very easily derived, on the basis that the *decrease* of oxidation number (i.e. the oxidation capacity) in the oxidizing system must equal the increase of oxidation number (i.e. the reducing capacity) of the system oxidized.

Oxidations (in acid solution)		Oxidant Required
Reactions	Amount Oxidized	
$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ +2 +3	56 gm. Fe	$\frac{1}{5} \text{KMnO}_4$ ($158/5 = 31.6$ gm.) $\frac{1}{6} \text{K}_2\text{Cr}_2\text{O}_7$ ($294/6 = 49.0$ gm.)
$\frac{1}{2}\text{H}_2\text{C}_2\text{O}_4 \rightarrow \text{H}^+ + \text{CO}_2$ +3 +4	45 gm. $\text{H}_2\text{C}_2\text{O}_4$ (reaction at 80°C.)	$\frac{1}{5} \text{KMnO}_4$ (31.6 gm.)
$\frac{1}{2}\text{H}_2\text{O}_2 \rightarrow \text{H}^+ + \frac{1}{2}\text{O}_2$ -1 0	17 gm. H_2O_2	$\frac{1}{5} \text{KMnO}_4$ (31.6 gm.)
$\text{I}^- \rightarrow \frac{1}{2}\text{I}_2$ -1 0	166 gm. KI	$\frac{1}{5} \text{KMnO}_4$ (31.6 gm.) $\frac{1}{6} \text{K}_2\text{Cr}_2\text{O}_7$ (49.0 gm.)
$\text{NO}_2^- + \text{H}_2\text{O} \rightarrow \text{NO}_3^- + 2\text{H}^+$ +3 +5	85 gm. KNO_2	$\frac{2}{5} \text{KMnO}_4$ (63.2 gm.)

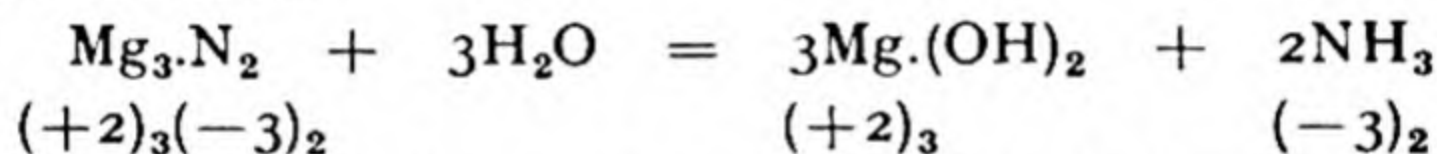
Analysis of Redox Changes. Oxidation numbers may be usefully applied to discern whether redox changes have occurred in a chemical reaction, and if so at what stage of the reaction. Compared with ammonia the base hydrazine, N_2H_4 (p. 437), is a very powerful reducing agent: its salts readily reduce copper salts to the metal in aqueous solution at ordinary temperature, while ammonia reduces copper oxide only at high temperature. Nevertheless oxidation numbers show that nitrogen is in a higher oxidation state in hydrazine:



and in fact hydrazine is prepared by the oxidation of ammonia (p. 437). Magnesium combines spontaneously with gaseous nitrogen at red heat to yield the nitride Mg_3N_2 , which is rapidly hydrolysed by water to give magnesium hydroxide and ammonia (p. 336):

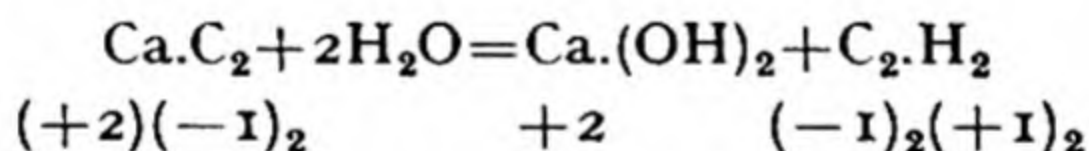


Hence in the formation of the nitride magnesium is oxidized and nitrogen reduced:



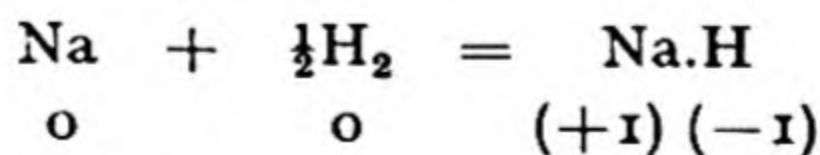
Evidently no redox change occurs in the hydrolysis.

Similar redox changes occur when calcium combines with carbon to give the carbide, CaC_2 (p. 345), and its hydrolysis contains no further redox change:

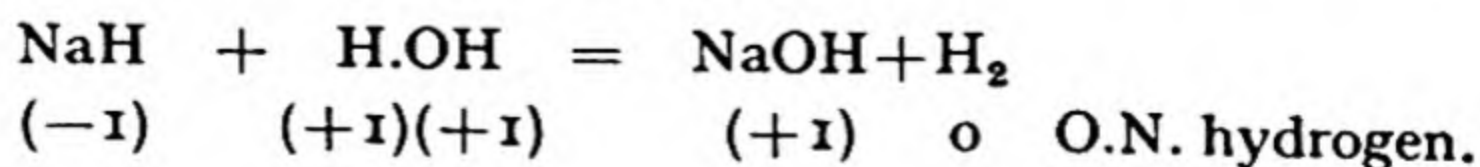


It will be seen that redox changes are completed during the formation of the nitride and carbide from their elements, and do *not* occur in the hydrolytic formation of ammonia or acetylene.

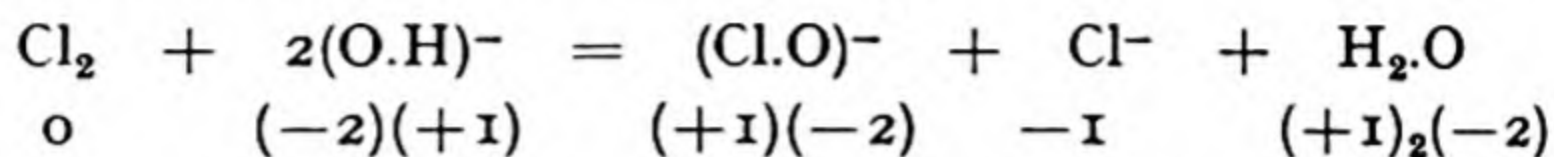
In the formation of sodium hydride from its elements (p. 280) sodium is oxidized and hydrogen reduced:



Water reacts with the hydride as follows:



In this hydrolysis one hydrogen atom from water oxidizes the hydrogen of the hydride to give molecular hydrogen. In the reaction of the halogens with alkalis, e.g.



the atoms of the halogen molecule behave differently; one is reduced to chloride ion (O.N. -1) and the second, in the hypohalite ion, is oxidized (O.N. $+1$).

CHAPTER XIX

THE COLLOIDAL STATE

Dialysis. If a bag made of pig's bladder, parchment, cellophane, or some similar material is filled with a solution of salt, sugar, or copper sulphate, and then surrounded by water, it is found that some of the solute passes through the membrane from the solution to the water. If, however, the bag is filled with a solution of glue, starch, or albumen, the solute does not pass through the membrane into the surrounding water. Salt and starch can therefore be separated from one another by making them up into a solution, placing the solution in a parchment bag, and suspending the bag in water; the salt gradually passes into the water while the starch does not.

This process was discovered about the middle of last century by GRAHAM, who described it as *dialysis*, i.e. 'a splitting-up [by passing] through.' Substances like glue, starch, and albumen, which cannot pass through the membrane, he called *colloids*, from

the Greek *kolla*, glue; and having observed that colloids were apparently amorphous in the solid state, while salt, sugar, and copper sulphate and other substances capable of penetrating the membrane were crystalline, he called the latter *crystalloids*. Advance of knowledge has shown that this division of substances into colloids and crystalloids is without scientific basis, for there is good reason to believe that all substances could be obtained in a colloidal form under suitable conditions. We therefore speak rather of the *colloidal state* of matter than of 'colloids' as a particular class of substances.

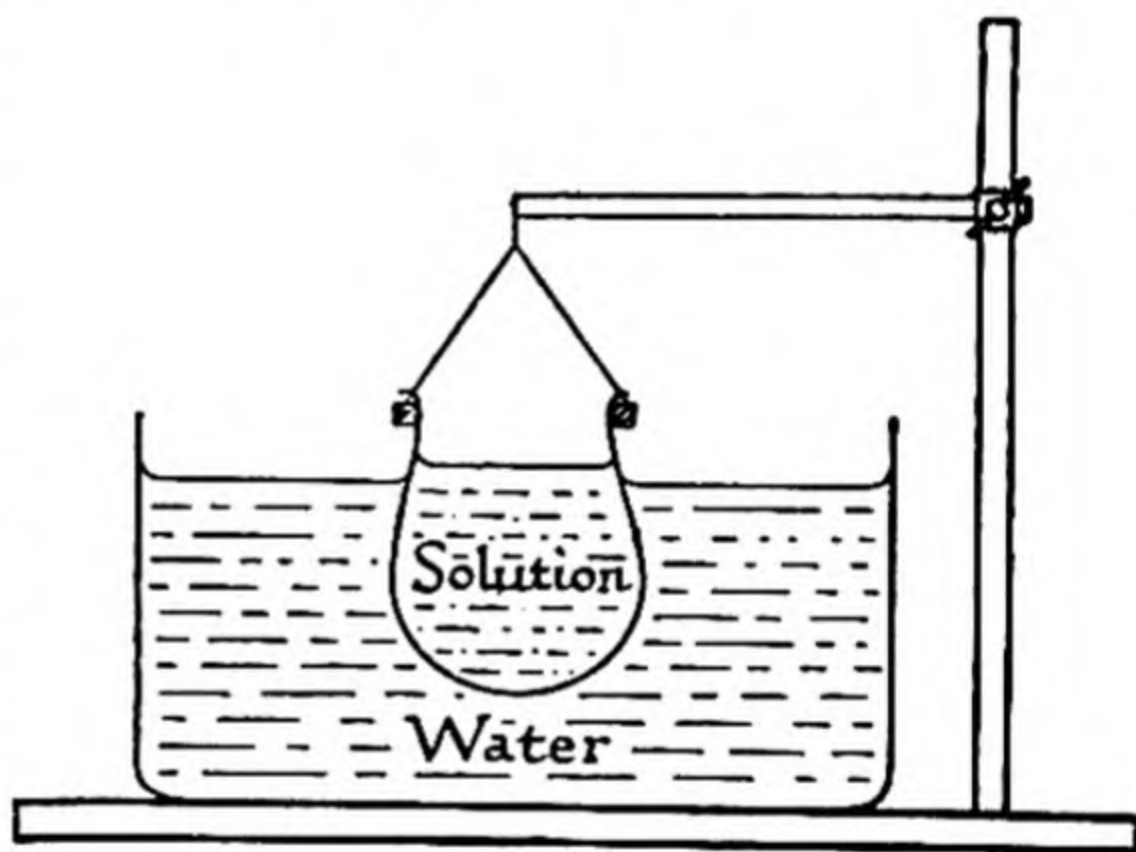


FIG. 50. DIALYSIS

Colloidal Solutions. A solution of starch differs from a solution of a 'crystalloid' such as salt in many important respects. For example, it shows a very small (but definite) osmotic pressure, it freezes and boils at almost exactly the same temperature as pure water, and its vapour pressure is very closely the same as that of pure water. Since the existence of an osmotic pressure, and an alteration in the vapour pressure, freezing-point, and boiling-point of a solvent, are caused by the presence of solute molecules (or ions) dissolved in the solvent, it seems that only very few such dissolved particles exist in a solution of starch. In other words, a so-called 'solution' of starch is not a true solution; yet it must contain starch, although no particles of starch are either visible or capable of removal by ordinary methods of filtration.

An obvious explanation of the paradox is that the starch exists in the form of molecular groups, so small as to be invisible and to pass easily through the pores of filter-paper, and yet so large as to have no appreciable effect upon the freezing- and boiling-points of the solvent and to cause very little osmotic pressure. A calculation will show that particles of a sufficient size to behave in this way might still be exceedingly small. Suppose a certain non-electrolyte to have a molecular weight of 60; 60 gm. dissolved in 1,000 gm. of water would depress the freezing-point by 1.86° (K for 100 gm. water = 18.6). Now suppose that the substance grouped itself into particles each consisting of 1,000 molecules. Then the depression—which is proportional to the number of solute *particles*—would be reduced to the almost negligible value of 0.00186° , but the

osmotic pressure, $\frac{22.4 \times 760}{1,000} = 17$ mm. Hg at 0° , would be easily

measurable, and could be used to determine the actual molecular weight of the particles (see p. 161). Molecules of M.W. 60 are so excessively minute that even an assemblage of 1,000 of them would be quite invisible, not merely to the naked eye, but under the highest power of the microscope. A gram-molecule of any substance contains about 6×10^{23} molecules; hence the weight of a 1,000-molecule

particle of a substance of M.W. 60 is approximately $\frac{60}{6 \times 10^{20}}$ i.e. 1×10^{-19} gm. How small this is will be realized if one remembers that the lowest weight used in everyday gravimetric analysis is 0.1 milligram, or 1×10^{-4} gm.

A colloidal solution may thus be regarded as a solution in which the particles of solute are too large to give rise to the normal osmotic pressure and allied effects, and yet so small as to be invisible and to remain in permanent suspension. Experiment has shown that, in most colloidal solutions, the diameter of the particles lies between

10^{-5} and 10^{-7} cm.; that is, between 100 $m\mu$ and 1 $m\mu$, where 1 μ = one thousandth of a millimetre (0.001 mm.) and 1 $m\mu$ (pronounced micro-mu) is one millionth of a millimetre (0.000001 mm.).

The smallest particles of matter visible even under high magnification have a diameter of not less than 0.0001 mm. Colloid particles are much smaller than this, and therefore cannot be actually viewed; they are, however, usually large enough to scatter light sideways, so that if a beam of light is passed through a colloidal solution, the path of the light may become visible. This is known as the *Tyndall effect* and is not observed in true solutions (though spectroscopically it can be demonstrated that true solutions show a similar behaviour in the *Raman effect*—in a very much lower degree). For the Tyndall effect to be observed in an aqueous colloidal solution, not only must the particles be of a suitable size relative to the wavelength of the light, but the *refractive index* of the material of the particles must differ greatly from that of water. It can be shown that the particles of starch, glue, etc., contain much loosely bound water (p. 261); hence the refractive index does not sufficiently differ from that of water for the Tyndall effect to be seen. Particles of oils, or of inorganic substances, however, readily exhibit the effect.

If a suitable colloidal solution, with a beam of light passing through it sideways, is viewed in an ultra-microscope against a dark background, it presents the appearance of a multitude of dancing points of light—much as a disorderly crowd of torch-bearers in a valley would appear, on a dark night, to a watcher on the mountainside above. Each point of light marks the position of one of the colloid particles, but the particles themselves—like the torch-bearers—remain invisible.

The irregular motion of the particles is an example of *Brownian movement*—a phenomenon so called because it was first observed, in 1827, by the English botanist BROWN. Brown noticed that pollen grains, when suspended in water, continually performed haphazard zigzag movements, which he was inclined to attribute to the agency of living organisms. Suspensions of other fine particles, such as those of gamboge and gum mastic, show the same erratic joggles, however, and WIENER realized that the cause lay in the bombardment of the particles by molecules of the solvent. The particles are, of course, being bombarded on all sides, but when by chance the collisions on one side of a particle outbalance those on the other, the particle will tend to move. It will rarely happen that the difference in 'push' is great, so that the Brownian movement will not be shown by large and heavy particles.

von Weimarn's Rule. When it was found that the diameters of colloidal particles are, as we have seen, usually between 10^{-7} and

10^{-5} cm., VON WEIMARN conceived the idea that any substance could be made to assume the colloidal state by obtaining it in particles of this approximate size. A likely method appeared to be to prepare the substance by precipitation—for then, initially, it exists as separate single molecules—but to prevent the molecules from aggregating together into particles of larger diameter than 10^{-5} cm. This object he was able to achieve in a large number of cases. For example, barium sulphate—a substance as different as possible from glue, starch, or other of Graham's 'colloids'—was obtained in a jelly-like colloidal form by mixing very concentrated solutions of barium thiocyanate and manganous sulphate, the precipitation being so rapid that the particles had time to grow to colloidal dimensions but no larger.

In the same way, a colloidal solution of calcium acetate may be made by adding a saturated solution of this salt to alcohol, in which it is insoluble, and which therefore precipitates it rapidly.

As a result of his researches upon the conditions necessary for obtaining precipitated particles of the required size, von Weimarn was able to show that the diameter of the particles is reduced by selecting a liquid in which the precipitate is *only very slightly soluble* and which is *viscous* rather than mobile, and by forming the precipitate from *very concentrated solutions* (von Weimarn's Rule).

Types of Colloidal Solution. The colloidal solutions hitherto considered have consisted of a liquid in which were scattered particles of an average approximate diameter of 10^{-5} to 10^{-7} cm.

<i>Dispersion Medium</i>	<i>Disperse Phase</i>	<i>Type of Colloidal Solution</i>	<i>Example</i>
Gas	Gas	Does not exist, since all gas mixtures are homogeneous	—
Gas	Liquid	Fogs	'November fog'
Gas	Solid	Smokes	Bonfire smoke
Liquid	Gas	Foams	Lather
Liquid	Liquid	EMULSIONS	Salad dressing
Liquid	Solid	SOLS	Colloidal silver
Solid	Gas	Solid foams	Cooked meringue

Here the liquid is known as the *dispersion medium* while the solid particles form the *dispersed substance*. From the point of view of the phase rule (p. 163), a colloidal solution is a heterogeneous system of two phases—the dispersion phase and the dispersed or disperse phase—in which the particles of the disperse phase are

invisible under the microscope but perceptible as points of light in the ultra-microscope.

It is clear that similar heterogeneous systems might exist of solid and liquid, liquid and liquid, liquid and gas, etc., and such systems are in fact described as colloidal dispersions. Some of the chief varieties, with examples, are shown in the table on p. 260.

Of these different kinds of dispersions, the most important are sols or *suspensoid colloids*, and emulsions or *emulsoid colloids*. Certain substances, like gelatine and glue, form colloidal solutions on mere admixture with water, and can be regained from the solutions by evaporation. These are known as *reversible* or *lyophilic* (hydrophilic) (i.e. solvent-attracted) colloids, in distinction from *irreversible* or *lyophobic* (i.e. solvent-repelled) colloids. The latter, when obtained from their colloidal solutions by evaporation or coagulation, cannot be directly reconverted into the colloidal state by simply mixing them with the dispersion phase. Examples of lyophobic colloids are metals, metallic oxides, and sulphides, and indeed most inorganic substances. It may be remarked that Nature, showing her customary aversion to definite frontiers, refuses to draw any hard and fast line between lyophobic and lyophilic colloids. Many so-called 'irreversible' colloids can be made to form colloidal solutions directly by a suitable adjustment of the conditions; but the distinction between the two classes is a useful conception in practice. As a rule, the particles of hydrophilic colloids themselves contain much loosely bound water, while those of lyophobic colloids are anhydrous. In general, irreversible sols are of the solid-in-liquid type, i.e. suspensoids, while reversible sols are of the liquid-in-liquid or emulsoid type; but there are many exceptions to this rule.

When a lyophilic sol is so concentrated as to become 'solid' or semi-solid, it is known as a *gel*. A typical gel is table jelly, 'soother than the creamy curd,' as KEATS describes it; * another is silica gel, which, when partially dried, is strongly hygroscopic and forms a very satisfactory desiccating agent—especially since, after use, it can be regained in its hygroscopic form by mere heating. Silica gel is also employed in certain works to carry the platinum catalyst in the contact process for the manufacture of sulphuric acid (p. 529). It may be obtained by adding concentrated hydrochloric acid, mixed with its own volume of water, to water-glass (p. 409).

Many gels share with silica gel the property of absorbing water (*imbibition*) and some of them, unlike silica gel, swell considerably in the process. The expansion can often take place against great external pressure—as much as 600 lb. to the square inch, i.e. 40 atmospheres—a fact which explains why tree roots may lift an

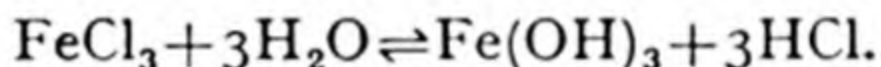
* Though SHAKESPEARE says, 'Out, vile jelly!'

asphalt pavement or push stones out of a wall. The living matter of the plant cells is a gel, and on absorption of water swells almost irresistibly.

Preparation of Colloidal Solutions. Since, in colloidal solutions, the particles of the disperse phase are intermediate in size between molecules and the fine particles of an ordinary 'suspension,' there are two obvious methods of preparing such solutions, viz. (a) the *aggregation method*, in which molecules, or small molecular aggregates, are caused to coalesce until they reach the required size, and (b) the *dispersion method*, in which larger particles are broken down to this size. Both methods are employed.

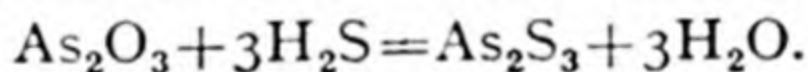
The *aggregation method* has already been illustrated in the account of von Weimarn's work. The essential point is that the substance required to assume the colloidal state should be rapidly produced or liberated in a dispersion medium in which it is only very slightly soluble. Some typical examples are as follows:

(i) *Ferric Hydroxide* may be obtained as a red sol by adding a few c.c. of concentrated ferric chloride to a large volume of nearly boiling water.



The solution is submitted to dialysis, to remove hydrochloric acid and some residual ferric chloride.

(ii) *Colloidal Arsenious Sulphide*. Hydrogen sulphide is passed through a cold aqueous solution of arsenious oxide (1 gm. in 100 c.c.):



The colloidal solution is a clear bright yellow; it will not keep for long unless excess of hydrogen sulphide is removed by the addition of a little extra arsenious oxide solution.

(iii) *Colloidal Sulphur* is an undesirable product in qualitative analysis, where it is often formed, for example, by the action of nitric acid upon hydrogen sulphide. It may be prepared as a milky white liquid by passing hydrogen sulphide into an aqueous solution of sulphur dioxide.

(iv) *Metals* can frequently be obtained in the colloidal state by the reduction of solutions of their salts with organic reducing agents. (Inorganic reducing agents are of less general application since, if electrolytes, they are likely to cause the metal to be precipitated in particles of larger than colloid dimensions; see p. 264). Thus, colloidal gold may be obtained as a red sol by the reduction of a neutral solution of gold chloride, AuCl_3 , with tannic acid. Colloidal silver may similarly be prepared by the reduction of dilute silver nitrate solution with an alkaline solution of dextrin; it is brown in colour. It may be observed here that the colour of colloidal solutions depends upon the size of the particles of the disperse

phase. The shorter waves of light, i.e. those towards the blue end of the spectrum, are scattered more than the longer ones; hence if the particles are very small, the solution will appear bluish by reflected light and red or brown by transmitted light.

(v) *Stearic Acid*. If a hot, concentrated, alcoholic solution of stearic acid is poured into water, in which the acid is only very slightly soluble, a colloidal solution is obtained in accordance with von Weimarn's rule.

The *dispersion method* may be illustrated by the colloid mill.

(vi) *The Colloid Mill*. This consists of two superimposed circular plates rotated at high speed in opposite directions. Into the narrow space between them, a suspension of the solid in the dispersion medium is gradually fed, and the grinding may at length be sufficient to bring the solid to colloidal dimensions. This operation is of considerable industrial importance.

(vii) *Bredig's Process*. If an electric arc is struck in pure water ('conductivity water,' p. 216) between two poles of a metal, the metal is often obtained in the form of a dilute colloidal solution. This method is very suitable for preparing colloidal platinum, gold, and silver (Fig. 51). The metal is vaporized in the arc, and then condensed to particles of colloidal size on rapid cooling: this method is therefore actually an *aggregation* method.

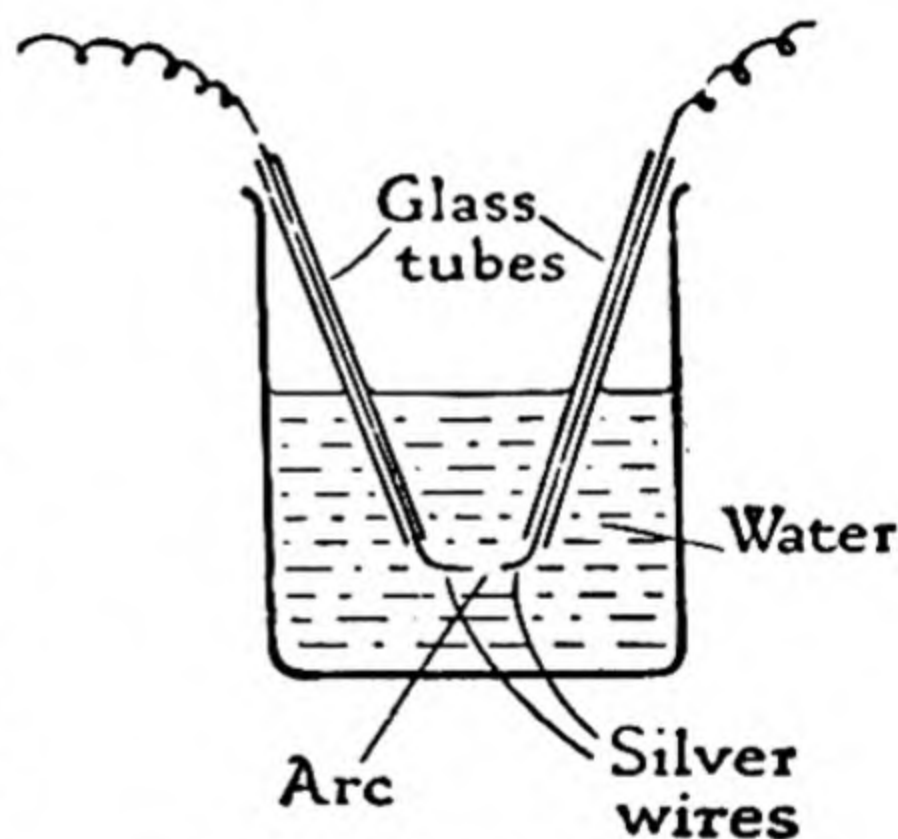


FIG. 51. BREDIG'S PROCESS

Colloidal solutions may sometimes be made (as with starch, glue, gelatine, albumen) simply by mixing the substance with warm water. In other cases, it is occasionally found that an insoluble substance will readily form a sol with water if a *trace* of an electrolyte is present. This change, compared somewhat fancifully with the digestive action of the stomach enzyme *pepsin* on proteins, is known as *peptization*. An example of peptization is the conversion of aluminium hydroxide into a sol by the addition to it of water containing a trace of hydrochloric acid. By the consequent formation of a small amount of aluminium ion, Al^{3+} , the particles can, by adsorption (see p. 264), again become electrically charged, and therefore dispersed.

Peptization may also be brought about by the addition of a lyophilic colloid. Thus colloidal graphite (as in 'deflocculated Acheson

graphite, p. 389) may be made by grinding graphite with an aqueous solution of tannin. It has been suggested by FINDLAY that the real hardship experienced by the Jews of Exodus in making bricks without straw is to be explained in the following way. Sun-dried bricks are crumbly unless made from colloidal clay. To convert clay into this state, a peptizer is necessary. This the Jews obtained by soaking straw in water, the infusion containing a lyophilic colloid with the required peptizing action.

Electrical Properties. The particles of the disperse phase of a lyophobic colloid are electrically charged, all with a charge of the same sign. This may be shown by the fact that if electrodes are placed in the cell and a potential difference set up between them, the particles all move slowly either to the cathode or to the anode—more often to the anode. This migration of colloid particles is known as *electrophoresis* (formerly *cataphoresis*).

Electro-positive colloids, i.e. those with positively charged particles, include ferric hydroxide, aluminium hydroxide, and the

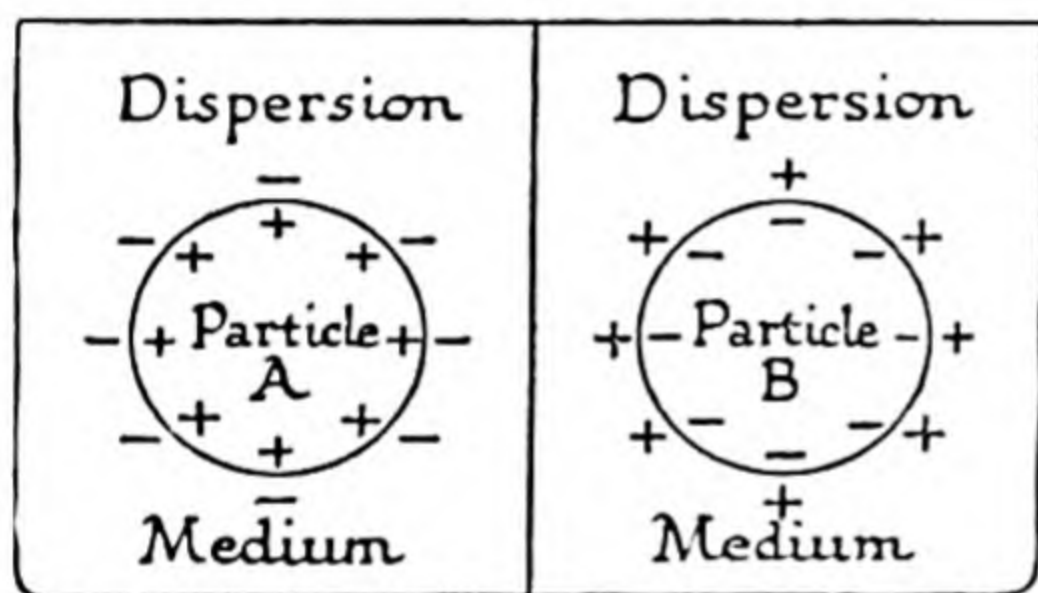


FIG. 52. CHARGES ON COLLOID PARTICLES. A, POSITIVELY CHARGED; B, NEGATIVELY CHARGED

red colouring-matter of blood (haemoglobin). Electro-negative colloids include gold, silver, platinum, silicic acid, sulphur, and arsenious sulphide.

If, in the above experiment, a porous diaphragm is placed in the sol between the electrodes, passage of the colloid particles is prevented, and water is forced towards whichever electrode the particles would *not* have approached. In this pro-

cess of *electro-osmosis*, the relative motion of disperse phase and dispersion medium is the same as in the electrophoresis of the same sol.

The origin of the charge carried by the particles of a lyophobic colloid is probably to be sought in a preferential adsorption of ions from the dispersion medium. If a particle adsorbs negative ions in preference to positive ions it becomes negatively charged, and vice versa. In any event, since the sol as a whole is electrically neutral, each particle must possess an electrical double layer (Fig. 52).

Coagulation and Precipitation. When an electrolyte is added to a lyophobic sol, the particles of the disperse phase coalesce into larger particles which appear as a precipitate. If, for example,

hydrochloric acid is added to arsenious sulphide sol, a precipitate is at once obtained. Sodium chloride or any other electrolyte may be substituted for the hydrochloric acid. The preferential adsorption of ions mentioned above can only occur when the ionic concentration in the medium is very small: as it becomes larger the preferential effect is lost, the particles lose any net charge, and are coagulated. The role of electrolytes as coagulants thus becomes clear (see below).

It has been found that the coagulating powers of many unipositive cations are approximately the same. Thus, expressing the coagulating power of potassium ion, K^+ , as 50, that of lithium ion, Li^+ , is 43, and that of sodium ion, Na^+ , is 49 under comparable conditions. This is what would be expected if the coagulation were indeed a purely ionic effect. Moreover, with bipositive ions, the coagulating power should be greater, since each ion carries a double charge; and this deduction is borne out in practice, though the relative effect could not be foreseen. Bipositive cations, in fact, have roughly a hundred times the coagulating power of unipositive cations, while tripositive ions are some 700 times as effective as the latter. This explains the use of alum—containing the tripositive aluminium ion Al^{3+} —to check the flow of blood from a cut. Blood, like many other natural liquids, is a sol in which the particles of the disperse phase are negatively charged; they are therefore rapidly coagulated by the tripositive aluminium ions.

The statement that *the coagulating power of an ion is a function of its electric charge* is known as the *Hardy-Schulze Law*.

A second way in which coagulation of a sol may be effected is to add to it another sol the particles of which are oppositely charged; for instance, a ferric hydroxide sol (+) will precipitate gold from a gold sol (—).

Protection. Lyophilic colloids are much more stable towards precipitating agents than are lyophobic colloids. In the case of aqueous sols, this may be caused by the formation of a shell of water round each colloid particle. The result of adding a lyophilic sol to a lyophobic sol is often to stabilize or 'protect' the latter to such an extent that it is no longer easily coagulated by electrolytes—possibly also a 'shell' effect, a lyophobic particle becoming surrounded by a shell of lyophile, which in turn is protected by its shell of water. However this may be, the fact of protection is turned to useful account in many ways, both in pure science and in industry and the arts.

An example of protection may be seen when dilute solutions of silver nitrate and sodium chloride, containing about 1 per cent of gelatin, are mixed. An opalescent liquid, consisting of a silver chloride sol, is formed instead of the usual curdy precipitate. The

silver bromide emulsion of the photographic plate or film is so produced.

Adsorption Indicators. In 1923, FAJANS showed that certain dyes can be used as indicators in various precipitation titrations, particularly the titration of silver nitrate against a chloride, bromide, or iodide. The dyes employed are mostly derivatives of fluorescein, and are known as *adsorption indicators*. The change in colour which they undergo at the end-point is produced in quite a different way from that which occurs in ordinary indicators in acid-alkali titrations.

When silver nitrate solution is run into a neutral solution of a chloride containing a few drops of fluorescein solution, the chloride solution shows the yellowish-green colour of aqueous fluorescein solutions up to the point of equivalence, and the precipitate of silver chloride remains white. Addition of the slightest excess of silver nitrate causes the *precipitate* (not the solution) to assume a pink colour. The colour change is reversible, addition of excess of chloride to the liquid causing the precipitate to turn white again.

An explanation of this phenomenon is as follows. When the silver chloride is first precipitated, it is partly colloidal, and it continues in this condition almost up to the point of equivalence. Colloid particles of electrolytes tend to adsorb their own ions, and while the chloride is in excess the particles of silver chloride are negatively charged with respect to the solution owing to the adsorption of chlorine ions to form a complex conventionally represented as $[\text{AgCl}]\text{Cl}^-$. This formula must not be taken to imply that the complex is of a definite and constant composition—it signifies merely that the precipitate of silver chloride has adsorbed chloride ions.

When excess of silver nitrate has been added to the solution, the particles of silver chloride give up their adsorbed chlorine ions, and adsorb silver ions instead, so that the complex $[\text{AgCl}]\text{Ag}^+$ is formed. This is positively charged with respect to the solution.

Fluorescein is a weak acid ($K \approx 10^{-8}$), and its anions are adsorbed by the complex $[\text{AgCl}]\text{Ag}^+$ to form silver fluoresceinate, which is red, on the surface of the precipitate. The complex $[\text{AgCl}]\text{Cl}^-$, however, which is negatively charged, does not adsorb the fluorescein anions. Hence the colour change on the precipitate does not occur until the silver nitrate solution has been added in excess; but since even a very slight excess is sufficient to effect it the end-point is very sharp.

Other acidic adsorption indicators are dichlorofluorescein, eosin (tetrabromofluorescein), and Rose Bengal (dichlorotetraiodofluorescein). Dichlorofluorescein is a stronger acid than fluorescein, and may therefore be used in the titration of chlorides in slightly acid solution; fluorescein can be employed only in neutral solution.

Eosin is suitable for the titration of bromides and iodides in neutral or acid solutions, but is unsuitable for the titration of chlorides since its anions are absorbed by the precipitate of silver chloride before the point of equivalence is reached.

Some basic adsorption indicators are known, e.g. rhodamine 6G. The mechanism of their action is similar to that of the acidic indicators, except that the effective ion is the cation.

PART II

CHAPTER XX

GROUP O

HELIUM, He; NEON, Ne; ARGON, Ar; KRYPTON, Kr;
XENON, Xe; RADON, Rn

(Physical constants are given in the table on p. 274)

History. In 1784 CAVENDISH was engaged upon an investigation of the behaviour of air subjected to continued sparking. He enclosed a volume of air in a tube over caustic potash solution, and observed that the passage of electric sparks produced brown fumes (NO_2) which dissolved in the potash; the volume of the air therefore diminished. After a time, no further diminution took place, and Cavendish then introduced a little oxygen ('dephlogisticated air') into the tube. Further sparking now produced a fresh loss in volume, and the process was repeated until, even after the addition of more oxygen, the passage of sparks was without effect. Cavendish next absorbed the residual oxygen by the introduction of a solution of liver of sulphur (potassium polysulphides) and found that a small bubble of gas was left. He estimated the volume of the bubble as not more than $\frac{1}{120}$ of the volume of nitrogen ('phlogisticated air') and seems to have suspected that it differed from the latter; though, very characteristically, he expresses himself with caution: 'If there is any part of the phlogisticated air of our atmosphere which differs from the rest . . . we may safely conclude that it is not more than $\frac{1}{120}$ part of the whole.'

More than a century later, LORD RAYLEIGH was working on the determination of the densities of gases, and in 1892 wrote to *Nature* as follows: 'I am much puzzled by some recent results as to the density of nitrogen, and shall be obliged if any of your chemical readers can offer suggestions as to the cause. According to two methods of preparation I obtain quite distinct values. The relative difference, amounting to about $\frac{1}{1000}$ part, is small in itself; but it lies entirely outside the errors of experiment, and can only be attributed to a variation in the character of the gas.'

Rayleigh's two sources of nitrogen were (a) atmospheric air, from which he removed successively, carbon dioxide, oxygen, and water-vapour, and (b) ammonia; and he found that the density of the atmospheric nitrogen was always appreciably greater than that of the nitrogen obtained from ammonia. For nearly two years the

problem remained unsolved, but in 1894 SIR WILLIAM RAMSAY suggested to Rayleigh that perhaps the discrepancy was due to the presence in the air of small quantities of a heavier gas not removed during the process of absorbing the carbon dioxide, oxygen, and water-vapour. The two investigators now joined forces, and it was found that, when atmospheric nitrogen is repeatedly passed over magnesium to form magnesium nitride, a residual gas is finally obtained which (*a*) is unaffected by magnesium, (*b*) has a volume of about 1 per cent of the original air, (*c*) has a spectrum different from that of nitrogen, and (*d*) has a density of nearly 20.

Cavendish's speculation was therefore justified, and the new gas was called *argon* (Greek, 'idle'), since it was discovered to be completely without chemical properties.

Ramsay wondered whether argon existed elsewhere than in the air, and while seeking for possible sources, he was reminded by MIERS that HILLEBRAND had obtained a gas, supposed to be nitrogen, by heating a rare mineral named cleveite. He at once sent out an assistant to buy a sample of cleveite, and put him on to the task of extracting the gas from it. Most of the gas proved to be nitrogen, but a small quantity of it could not be removed (as ammonia) by sparking with hydrogen over sulphuric acid; this residue Ramsay himself examined. When he found that its volume could not be reduced by sparking with oxygen over caustic soda, and that its spectrum appeared to be peculiar, he sent a specimen of it to SIR WILLIAM CROOKES, whose experience of spectroscopy was much greater than his own. For a week, Crookes was too busy to attend to the matter, but on 23rd March 1895 he telegraphed that the new gas was *helium*, an element discovered spectroscopically on the sun * by SIR NORMAN LOCKYER in 1868, but unknown upon the earth before Ramsey had thus dramatically found it. Ramsay was pardonably excited; he even wired to the French chemist BERTHELOT desiring him to communicate the news to the Académie des Sciences on the following Monday, while all his research students dashed round London to buy up more cleveite.

Helium proved to be just as chemically inactive as argon, and since neither gas could be fitted into an existing group of the periodic system, Ramsay's imagination took a daring flight and conceived Group O. But two gases were not enough to fill a group, and the search for others to accompany them was set in hand. With the assistance of M. W. TRAVERS and others, he examined the few cubic centimetres of liquid left when about a litre and a half of liquid air had been allowed to evaporate away almost completely, and discovered a third inactive gas, namely *krypton*.† Later, two more

* Hence its name, from the Greek *hēlios*, the sun.

† Greek, *hidden*. Cf. *crypt*.

members of the group, *neon** and *xenon*,† were isolated from the air, and when the gas given off by radium was closely investigated it was found to contain, besides helium, a short-lived radioactive element, *radon*, which occupied the last place in the new family.

The proportions in which the rare gases exist in the atmosphere are as follows:

<i>Gas</i>	<i>Proportions by Volume</i>	<i>Proportions by Weight</i>
Helium	1 part in 200,000	1 lb. in 725 tons
Neon	1 part in 65,000	1 lb. in 44 tons
Argon	93 parts in 10,000	1 lb. in 75 lb.
Krypton	1 part in 1,000,000	1 lb. in 173 tons
Xenon	1 part in 11,000,000	1 lb. in 1,208 tons

They may be extracted from the air during its liquefaction and distillation, but helium is principally obtained from the natural gas issuing from the earth in Kansas, Texas, Utah (U.S.A.), and Medicine Hat (Canada). This gas contains up to 1 per cent of helium, and is so abundant that the price of helium is now no more than $1\frac{1}{2}d.$ per cubic foot.‡ The U.S.A. alone produces 50,000 cubic feet daily.

Properties. The electronic constitutions of the inert elements are shown in the table. The Roman numerals indicate the series of the Periodic System, terminated successively by an inert element: beneath appear the orbitals progressively occupied with electrons by the range of elements in the series. Comparison with Fig. 28, p. 92, indicates that this occupancy has reached its maximum in the inert elements, and it is for this reason that they each terminate a series. The whole electronic content of the atoms must therefore be paired in spin, and the valency in the normal state is consequently zero (p. 107).

<i>Series</i>	I	II	III	IV		V	
<i>Orbitals</i>	1s	2(s, p)	3(s, p)	3d	4(s, p)	4d	5(s, p)
Helium	2						
Neon	2	8					
Argon	2	8	8				
Krypton	2	8	8	10	8		
Xenon	2	8	8	10	8	10	8

* Greek, *new*. The author may be excused for mentioning that, with great generosity, Professor Travers presented a discharge-tube containing some of the original specimen of neon to the Clifton College Science Department.

† Greek, *the stranger*.

‡ In the U.S.A.

The physical constants of the group are given in the following table:

<i>Gas</i>	<i>Atomic Number</i>	<i>Atomic Weight</i>	<i>M.P.</i>	<i>B.P.</i>
Helium, He	2	4.003	-272.2°	-268.9°
Neon, Ne	10	20.183	-248.7°	-246.0°
Argon, Ar	18	39.944	-189.3°	-185.2°
Krypton, Kr	36	83.80	-157°	-152.3°
Xenon, Xe	54	131.3	-112°	-108.1°
Radon, Rn	86	222	-71°	-65°

All members of the group are monatomic.

Uses. In spite of their unreactive nature, the rare gases have already won great industrial importance. *Helium* is only very slightly soluble in water (0.0097 c.c. per c.c. of water at 0°) and is therefore employed in making an artificial atmosphere for divers. In order to supply air to a submerged diver, it has to be pumped down to him at a pressure exceeding the hydrostatic pressure at the depth at which he is working. Under these conditions, much nitrogen dissolves in his blood, and when he returns to the surface, the excess of nitrogen comes out of solution and may cause an embolism, i.e. a stoppage in the circulation of the blood, perhaps with fatal results. By using an artificial air of oxygen and helium this danger is avoided, since the solubility of helium is so small.

Helium, *neon*, and *argon* emit a coloured light when a high-voltage discharge is passed through them at low pressure, and are therefore widely employed in advertisement signs. Neon gives a beautiful reddish-orange glow; argon, in the presence of mercury, gives a blue glow, which, seen through an amber tube, appears green; and helium gives a nearly white light, which appears golden through a yellow tube.

Argon is used in certain rectifiers, to obtain direct current from alternating current; but its principal application is as the gas in gas-filled electric filament lamps, of which it greatly increases the life and efficiency. *Krypton* and *xenon* are even better for this purpose, and will doubtless replace argon entirely. It has been calculated that the U.S.A. alone will save \$200,000,000 a year in its electric light bill when this substitution is effected.

CHAPTER XXI

HYDROGEN, H

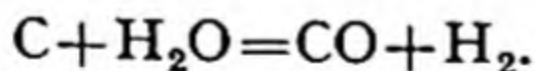
Atomic number: 1. *Atomic weight:* 1.0080. *Density:* 0.0899 gm. per litre at N.T.P. *Melting-point:* -259.2° . *Boiling-point:* -252.8° .

History. Hydrogen was first recognized to be distinct from other gases by CAVENDISH in 1766, who prepared it by the action of dilute sulphuric acid or dilute hydrochloric acid upon iron. The name 'hydrogen' (Greek, 'water-producer') was conferred upon it by LAVOISIER, after the discovery that it was a constituent of water.

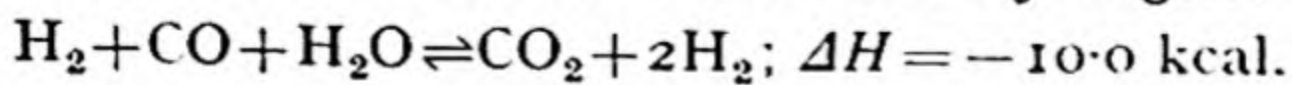
Occurrence. Free hydrogen occurs in the atmosphere of the sun and of similar celestial bodies, but the uncombined element is found only in traces upon the earth, e.g. in volcanic gases, in the atmosphere (in *very minute* proportion), and in certain rocks. Hydrogen compounds, on the contrary, are numerous, abundant, and widely distributed. *Water* contains 11.1 per cent by weight of hydrogen; *petroleum* consists of mixtures of hydrocarbons, C_xH_y ; *sugar*, *starches*, and most animal and vegetable products contain hydrogen; and large quantities of hydrogen, in the form of *bicarbonates*, are present in temporarily hard water.

Manufacture. Although hydrogen is obtained as a by-product in many commercial processes, e.g. the electrolytic manufacture of sodium hydroxide (p. 289), the demand for it is so great that such sources are entirely inadequate. Hydrogen nowadays, in fact, ranks as one of the 'heavy chemicals,'* and many industrial methods of obtaining it are worked on a very large scale.

(i) *The Bosch Process.* By far the most important of these methods is that invented by the German chemist BOSCH, in which *water-gas* (p. 396) is made to react catalytically with steam. When steam is blown over white-hot coke, a mixture of carbon monoxide and hydrogen is formed:



This mixture is known as water-gas. In the presence of suitable catalysts, and at suitable temperatures, water-gas and steam may be made to react to form carbon dioxide and hydrogen:

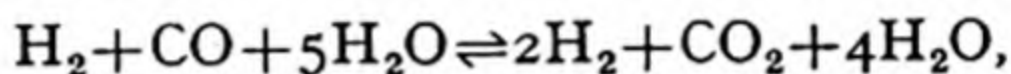


* i.e. those chemicals which are manufactured in large quantities, as opposed to the 'fine' chemicals such as dyes and drugs.

The reaction is reversible and the equilibrium condition is expressed by the equation (p. 128):

$$K = \frac{[\text{H}_2][\text{CO}_2]}{[\text{H}_2\text{O}][\text{CO}]}$$

The value of the constant, K , varies with the temperature. At 500° it is 10, whence it is easily possible to calculate the proportions in which the steam and water-gas must be mixed in order to keep the percentage of unchanged carbon monoxide in the residual gas as low as desired. In practice, 2 per cent of carbon monoxide, after condensation of the excess steam, represents an average figure. Hence, from the equilibrium equation at 500° , 1 volume of water-gas containing 50 per cent of carbon monoxide must be mixed with $2\frac{1}{2}$ volumes of steam:



for then, in the issuing gases, $\frac{[\text{H}_2]}{[\text{H}_2\text{O}]} \simeq \frac{1}{2}$ whence $K = \frac{1}{2} \times \frac{[\text{CO}_2]}{[\text{CO}]}$, or

$10 = \frac{[\text{CO}_2]}{2[\text{CO}]}$. That is, the volume of the residual carbon monoxide will be about 5 per cent of the volume of carbon dioxide, and hence about $\frac{5}{3}$, or roughly 2, per cent of the issuing gases after condensation of the steam.

Since the reaction between water-gas and steam is exothermic (see p. 275), it will proceed spontaneously once started, as long as the heat produced is efficiently employed, by means of heat-interchangers, to keep the reaction-tubes at the working temperature. Actually the mixture of water-gas (1 volume) and steam ($2\frac{1}{2}$ volumes) is passed through a converter maintained at about 500° and containing a catalyst; this consists mainly of finely divided iron, produced *in situ* by the reducing action of the gases upon ferric oxide, Fe_2O_3 , initially introduced. The hot gases leaving the converter are passed into the heat-interchangers to heat the incoming gases, and are then freed from carbon dioxide by scrubbing with water under pressures of 25 to 30 atmospheres. The residual carbon monoxide, and remaining traces of carbon dioxide, are removed by a preliminary scrubbing with ammoniacal cuprous formate or carbonate under high pressure, followed by a second scrubbing with concentrated sodium hydroxide solution at about 250° . The only impurity left in the hydrogen in quantity is now water, and this is removed by freezing at high pressure and subsequent passage of the gas through a dehydrating agent.

(ii) *Coke-oven Process.* The gas obtained in the manufacture of coke (p. 395) is a mixture of about 50 per cent of hydrogen with 28

per cent of methane, 9 per cent of nitrogen, and small quantities of carbon monoxide, carbon dioxide, acetylene, ethylene, and benzene. It is washed with ammonia solution to remove most of the carbon dioxide, and then with water and sulphuric acid, after which it is compressed to 10 atmospheres and subjected to a gradual refrigeration by means of liquid nitrogen. Benzene and acetylene are liquefied first, and are removed. The temperature is then lowered in successive stages, to liquefy the ethylene, methane, carbon monoxide, and nitrogen, after removal of which the hydrogen is left in a sufficiently pure state for commercial use.

(iii) *Electrolysis.* In countries with abundant water-power, e.g. Scandinavia and Switzerland, electrical energy is cheap, and is therefore used to prepare hydrogen by the electrolysis of water. In less fortunate countries this method is generally far too expensive—especially as the production of one ton of hydrogen is accompanied by the production of eight tons of oxygen, for which the market is very small.

Uses. The principal uses of hydrogen are in the synthesis of ammonia (p. 429) and the manufacture of methyl alcohol (p. 402).

Another important industrial application of hydrogen is in the hydrogenation, or 'hardening,' of vegetable and animal oils. These oils, e.g. whale oil, arachis (peanut) oil, and cotton-seed oil, are closely related to the solid fats, the main difference lying in the fact that the oils contain a somewhat smaller proportion of hydrogen than the fats. It was discovered in 1902 by SABATIER that substances of this kind could be made to combine directly with hydrogen if gently heated in a current of the gas in the presence of metallic nickel as catalyst. This observation was the germ of what has now reached the dimensions of a large industry. On the industrial scale the catalyst is prepared by first superficially oxidizing nickel turnings, gauze, or wire electrolytically, and subsequently reducing the oxide in hydrogen. The nickel is then packed into tubes, arranged in series, through which a stream of the oil is passed against a counter current of hydrogen; the usual temperature is about 180° , and since the reaction takes only a few minutes a small plant can give a large output. Other interesting methods of preparing finely divided nickel as catalyst include: (a) the decomposition of nickel carbonyl, $\text{Ni}(\text{CO})_4$, p. 601; (b) treatment of an alloy of nickel and aluminium with aqueous sodium hydroxide (giving 'Raney nickel,' named after the inventor); and (c) the self-reduction of nickel formate on heating.

The hydrogenated oils so obtained set to a solid fat on cooling and are therefore said to have been 'hardened.' Hardened whale oil is largely used in the manufacture of soap and candles, while hardened vegetable oils form the basis of much margarine and

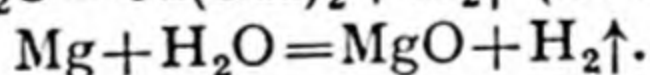
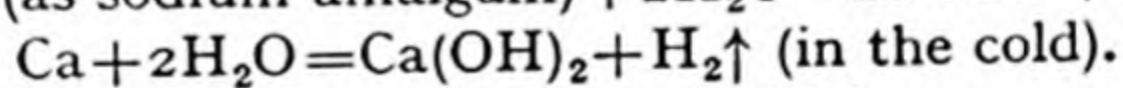
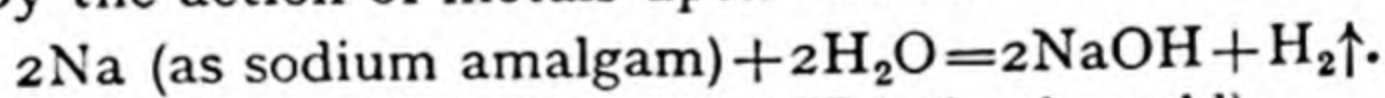
'artificial lard.' The latter products are perfectly wholesome, but lack vitamins A and D, which are contained in butter and are essential to health. The principal margarine manufacturers now produce 'vitaminized margarines,' adding in a concentrated form the vitamins extracted from cod and halibut liver oils, etc.

Hydrogen is also used to inflate balloons, but owing to its dangerous inflammability is replaced for this purpose, where possible, by the non-inflammable helium (p. 273). Small quantities of hydrogen are required for the oxyhydrogen and atomic hydrogen (p. 281) blowpipes.

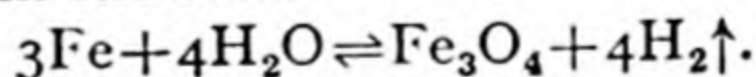
Laboratory Preparation. (i) Pure hydrogen can be prepared by the electrolysis of a hot solution of barium hydroxide in distilled water. The choice of barium hydroxide as electrolyte is made because any carbon dioxide absorbed from the air is precipitated as barium carbonate, and thus products formed from carbonate by electrolytic reduction cannot contaminate the hydrogen. Apart from water-vapour, the only impurity in the hydrogen (which is liberated at the cathode) is a little oxygen which has diffused back in solution from the anode. The gas is therefore passed over heated palladium, on the surface of which the oxygen is catalytically reduced to water. The hydrogen is then dried over phosphorus pentoxide.

Hydrogen of varying degrees of purity may be prepared in a great number of ways:

(ii) By the action of metals upon water:

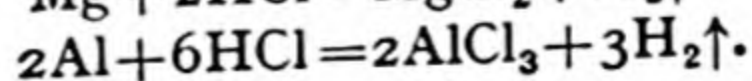
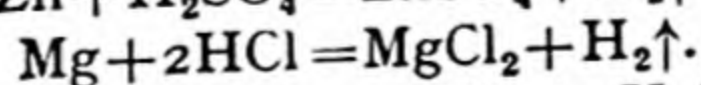
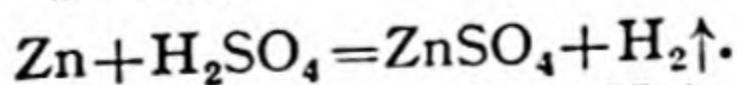


The magnesium should be heated in steam. Magnesium amalgam, however, will react in the cold.

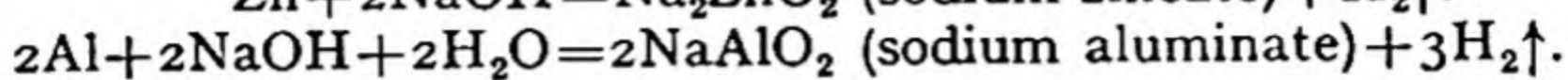
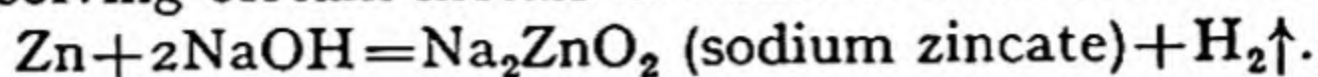


Steam is passed over white-hot iron.

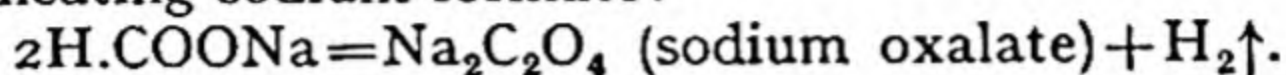
(iii) By the action of dilute acid (excluding such powerfully oxidizing acids as nitric acid) on metals above hydrogen in the electrochemical series (p. 244):



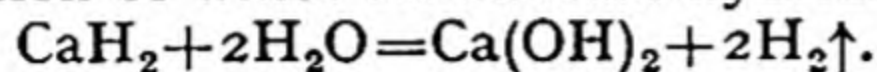
(iv) By dissolving certain metals in caustic alkali solution:



(v) By heating sodium formate:



(vi) By the action of water on calcium hydride:



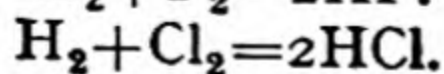
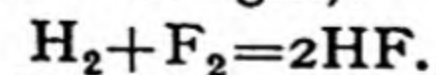
As prepared from impure commercial zinc and dilute sulphuric acid, hydrogen is liable to contain the following impurities: *arsine*, AsH_3 , from arsenic in the zinc or acid; *hydrocarbons*, such as acetylene, from carbides in the zinc; *hydrogen sulphide*, H_2S , formed by reduction of the sulphuric acid; and, of course, *moisture*. It may be purified by bubbling the gas through potassium permanganate solution, which oxidizes the hydrogen sulphide, hydrocarbons, and most of the arsine; then through silver nitrate solution to remove the remaining arsine; and finally through calcium chloride tubes, to dry it. But any sensible person would choose a different method to prepare the *pure* gas.

Pure zinc, now freely available commercially, has practically no action on pure dilute sulphuric acid; it will, however, dissolve readily if a drop or two of copper sulphate solution is added.

Properties. Hydrogen is a colourless, odourless, tasteless gas, non-poisonous but unable to support respiration. It is the least dense substance known, one litre weighing only 0.0899 gm. at N.T.P. It can be condensed to a colourless liquid, which boils at -252.8° and freezes to a white crystalline solid at -259.2° . Liquid hydrogen has the astonishingly low density of 0.071 gm. per c.c.

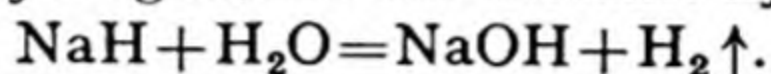
Hydrogen is only slightly soluble in water, 1 c.c. of water dissolving 0.02 c.c. of the gas at room temperature; it is, however, readily absorbed, or *occluded*, by certain metals, e.g. iron, platinum, and particularly palladium. If red-hot palladium is allowed to cool to room temperature in an atmosphere of hydrogen, it absorbs 935 times its own volume of the gas. The hydrogen appears to be contained in the palladium partly in solid solution and partly as the definite compound Pd_2H , *palladium hydride*. On heating, all the hydrogen is given up again. As a consequence of occlusion, hydrogen will pass through the walls of a palladium vessel, and, at high temperatures, through the walls of iron and steel tubes.

At ordinary temperatures hydrogen will combine spontaneously only with fluorine (even in the dark and at very low temperatures) and chlorine (in the presence of light):

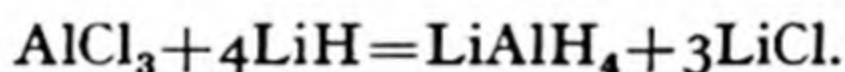


It will, however, also combine spontaneously with oxygen, without previous heating, if a mixture of the two gases is passed through platinum sponge or over platinum black. Hydrogen takes fire when heated in the air to about 634° , burning with a colourless flame consisting of two cones only—an inner cone of unburnt gas and an outer cone of complete combustion. Mixtures of hydrogen and air, and hydrogen and oxygen, explode violently if ignited. The temperature of combination is greatly raised if the gases are thoroughly dry, and the combustion then takes place quietly.

Hydrogen combines with lithium, sodium, and potassium on heating, to give colourless, crystalline hydrides, LiH , NaH , KH . Similar compounds, CaH_2 , SrH_2 , and BaH_2 , are given by the alkaline-earth metals calcium, strontium, and barium. On addition of water, they yield hydrogen, and the metallic hydroxide:



All these hydrides are ionic compounds, e.g. Li^+H^- , and have crystal structures analogous with NaCl and Ca(OH)_2 respectively; on electrolysis of a fused mixture of lithium hydride and chloride, hydrogen is released at the *anode*. The radius of the hydrogen anion (1.27 \AA .) is only slightly less than that of fluoride (1.33 \AA ., p. 144). Lithium hydride and aluminium chloride interact in ether solution to give the powerful reducing agent lithium aluminium hydride, LiAlH_4 , now widely used to prepare other hydrides (pp. 373, 407):



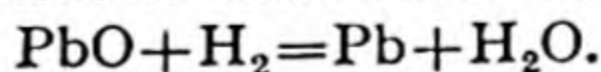
The hydrides of certain other metals, such as tin, antimony, and bismuth, are *covalent* in constitution, and are prepared by indirect means.

When hydrogen is passed slowly through boiling sulphur, a little hydrogen sulphide is formed:



Ammonia may be synthesized by the direct combination of nitrogen and hydrogen under pressure and in the presence of a heated catalyst (p. 429), while if carbon is strongly heated in hydrogen various hydrocarbons, such as methane, CH_4 , and acetylene, C_2H_2 , are formed.

In the laboratory, hydrogen is often used as a reducing agent, e.g. for converting many metallic oxides into metals:



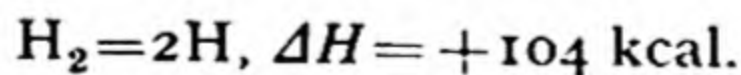
In the presence of reduced nickel as catalyst it is an excellent agent for the reduction of organic compounds (see Uses, p. 277).

Nascent Hydrogen. The reducing powers of hydrogen are often temporarily much greater during its actual liberation in a chemical reaction. Hydrogen in this condition is described as 'nascent'

(i.e. just born), and mixtures producing it are often able to effect reductions that the gaseous element cannot. For example, if gaseous hydrogen is passed through potassium chlorate solution, no action takes place; but if the solution is acidified and magnesium is added, the chlorate is quickly and smoothly reduced to the chloride. Ferric chloride in solution, again, is unaffected by gaseous hydrogen, but is reduced to ferrous chloride by zinc and dilute sulphuric acid. It was at one time believed that 'nascent' hydrogen was hydrogen in the form of single atoms, which are known to be more active than the diatomic molecules. It must be recognized that the reducing agent is not simply hydrogen, but the system hydrogen-metal, and the condition of the hydrogen when 'nascent' must correspond to an intermediate stage between the discharge of hydrogen ions at the metal surface, and the release of molecular hydrogen from the surface (p. 247).

Atomic Hydrogen. Hydrogen in its diatomic form can be made to dissociate into single atoms, the degree of dissociation depending upon the conditions. When hydrogen is passed at very low pressure through an ozonizer, the issuing gas contains a small percentage of atomic hydrogen, and possesses strong reducing powers; it will, for instance, reduce silver chloride to silver, lead nitrate to lead, barium sulphate to barium sulphide, and sulphur to hydrogen sulphide, without the application of external heat; nitrogen, on the other hand, remains unaffected by it.

A better method of obtaining atomic hydrogen is due to LANGMUIR. It consists in blowing a current of hydrogen through an electric arc struck between tungsten electrodes, and gives a yield of about 10 per cent H at $3,000^{\circ}$. The dissociation is strongly endothermic:



so that when the atoms recombine to form diatomic molecules, great heat is evolved. This is the principle of the atomic hydrogen blowpipe (Fig. 53). The stream of gas is projected on to the object to be heated, which is held a short distance away from the arc; and when the atoms reunite on the surface of the object, temperatures sufficiently high to melt tungsten ($3,400^{\circ}$), tantalum, and many

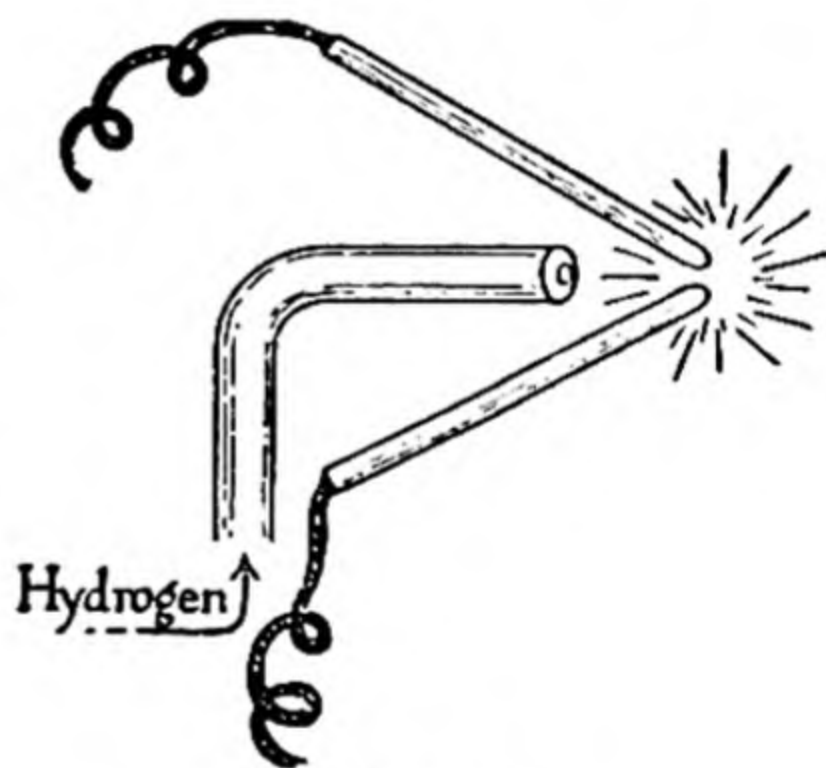
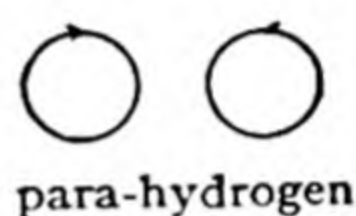


FIG. 53.
ATOMIC HYDROGEN BLOWPIPE

other highly refractory substances are obtained. It will be observed that no oxygen is supplied—though naturally the hydrogen burns in the surrounding atmosphere—and the strong reducing-power of the atomic hydrogen flame is a great advantage in those cases where it is particularly desirable to avoid oxidation of the heated substance.

Allotropy of Hydrogen. Hydrogen exists in two allotropic forms, *ortho*-hydrogen and *para*-hydrogen, the gas at ordinary temperatures being an equilibrium mixture of the two allotropes, with the *ortho* form in preponderance (3 : 1). *Ortho*-hydrogen and *para*-hydrogen are identical in chemical properties, but differ slightly in their physical constants (e.g. M.P., B.P., specific heat). The difference between them is accounted for as follows. Like an electron (p. 93) a proton possesses a spin motion. In *ortho*-hydrogen, the nuclei of the two atoms composing the molecule are spinning in the same direction; in *para*-hydrogen they are spinning in opposite directions:



Deuterium, Heavy Hydrogen, D. By the method of the mass-spectrograph (p. 47), ASTON obtained a value 1.0078 for the atomic weight of hydrogen, on the standard $O=16.0000$, and this agreed with the value determined chemically. In 1929, however, GIAUQUE and JOHNSTON discovered that oxygen is a mixture of the isotopes (p. 99) O^{16} , O^{17} , and O^{18} , and, from a calculation based on the relative abundance of these isotopes, it was shown that the atomic weight of ordinary oxygen is not 16.0000 but 16.0035. Hence the chemical atomic weight of hydrogen is $\frac{1.0078 \times 16.0035}{16.0000}$, i.e.

1.0080, which is not in agreement with ASTON's physical value. It was suggested by BIRGE and MENZEL that the discrepancy might be caused by the presence in ordinary hydrogen of an isotope of mass 2, in such small quantity that it had been overlooked in the physical method. Search was made for this isotope by UREY and others, and its discovery was announced in 1931; it was called *deuterium*, D. In the following year, UREY and WASHBURN found that on the electrolysis of ordinary water (which contains both hydrogen oxide and deuterium oxide) hydrogen oxide was electrolysed at a greater rate than deuterium oxide, and by decomposing large quantities of water they were able to obtain a residue of pure deuterium oxide or 'heavy water,' D_2O . Some idea of the labour involved may be gathered from the fact

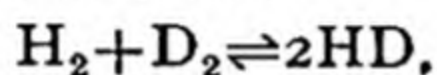
that, to obtain 1 c.c. of pure D_2O , it is necessary to electrolyse 100 gallons of water. It is, however, possible to purchase deuterium oxide from the chemical dealers as one would any other chemical.

Deuterium oxide differs considerably from hydrogen oxide in many of its physical properties, as shown in the following table:

	H_2O	D_2O
<i>Boiling-point</i>	100°	101.4°
<i>Melting-point</i>	0°	3.8°
<i>Density at 20°</i>	0.998	1.106
<i>Temperature of max. density</i>	4°	11.6°
<i>Ionic product at 25°</i>	10^{-14}	1.8×10^{-14}

Chemically, deuterium oxide is closely similar to hydrogen oxide, though slight differences in the biological effects of the two liquids have been reported.

Deuterium itself, D_2 , can be obtained by the electrolysis of deuterium oxide, in which pure phosphorus pentoxide has been dissolved. It is a colourless, inflammable gas, practically identical with hydrogen in all chemical properties, but slightly less reactive. With hydrogen it reacts as follows:

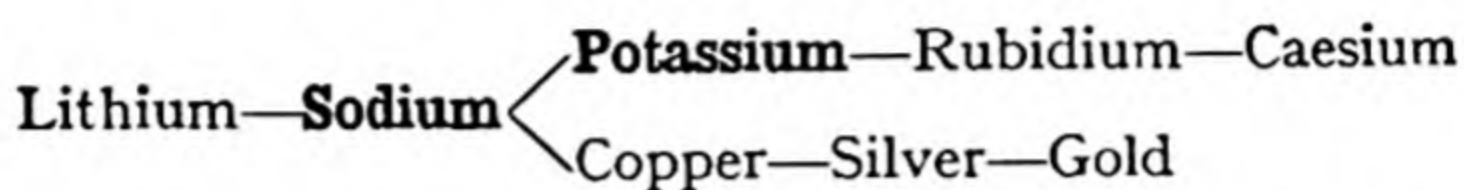


an equilibrium being set up.

CHAPTER XXII

GROUP I

SODIUM, POTASSIUM



The Alkali Metals. The typical elements of Group I, viz. lithium and sodium, together with Sub-group A, viz. potassium, rubidium, and caesium, are known as the *alkali metals*.

The alkali metals are closely similar to one another, and are the most reactive of all metals. They are strongly electropositive, and occur almost invariably as unipositive ions.

SODIUM, Na

Atomic number: 11. *Atomic weight:* 22.991. *Specific gravity:* 0.97.
Melting-point: 97.5. *Boiling-point:* 880°.

History. Ingenious scholars tell us that *sodium*, the metal in *soda*, really means 'headache metal.' *Soda* is the Arabic for a splitting headache, whence the white solid (Na_2CO_3) used to alleviate headaches came in medieval Europe to be called *sodanum*; and from this is derived our use of the word *soda* to denote sodium carbonate. The Hebrew word for naturally occurring sodium carbonate was *natron*, meaning 'the bubbly (mineral)'—a reference to its behaviour with a dilute acid (Prov. xxv. 20). From *natron* came the 'Latin' name *natrium* for the metal, and the symbol Na.

Such compounds of sodium as the chloride and carbonate have been known since prehistoric times, but were often confused with other salts. The first to distinguish clearly between soda (Na_2CO_3) and potash (K_2CO_3) seems to have been the accomplished Persian physician ABU MANSUR MUWAFFAK (tenth century A.D.). Both substances were extracted from plant ashes by the Arabs, who described them together as *al-qali*, 'the ash,' a word now familiar as *alkali*.

KERR (1755–1813) suspected that caustic soda (NaOH) and caustic potash (KOH) were metallic compounds, but the metals themselves

were first isolated in 1807 by DAVY. Davy placed a piece of moist caustic potash on an insulated platinum disk, connected to the negative terminal of a powerful electric battery. A platinum wire, connected to the positive terminal, was then brought into contact with the caustic potash, when a vivid action took place and globules of metallic potassium were formed on the cathode. 'Capital experiment,' wrote Davy in his note-book. A few days later he prepared sodium in a similar way.

Occurrence. On account of its great reactivity sodium is not found in nature as the free element. There are also comparatively few natural compounds of sodium, but of those which do occur, two exist in vast quantities, viz. *sodium chloride*, or *common salt*, NaCl ,

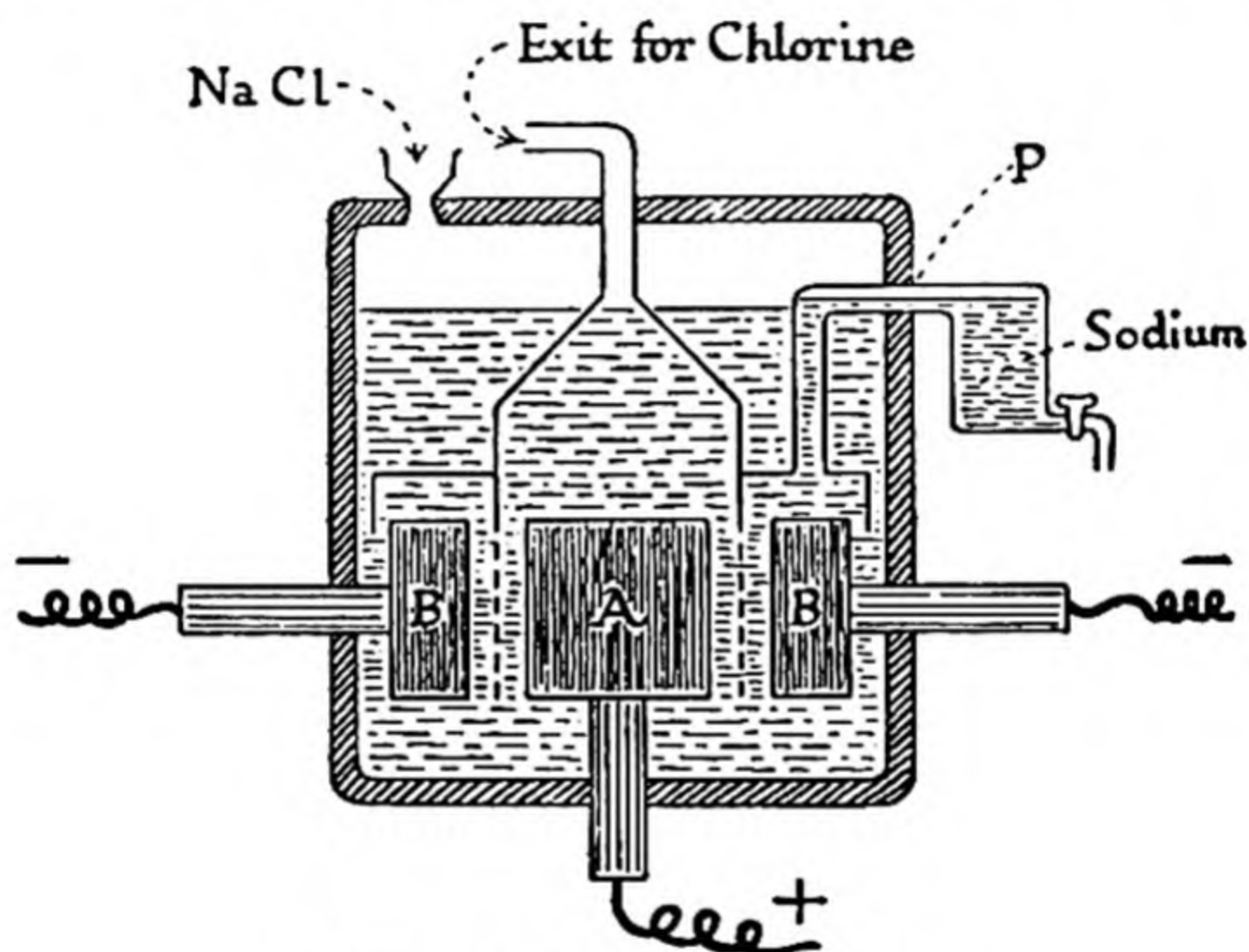


FIG. 54. THE DOWNS CELL

and *sodium aluminium silicate*, or *sodium felspar*, $\text{NaAlSi}_3\text{O}_8$, a constituent of soils. Smaller, but still large, amounts of *sodium nitrate*, or *Chile saltpetre*, NaNO_3 ; *sodium sesquicarbonate*, *natron*, or *trona*, $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$; *gay-lussite*, $\text{Na}_2\text{CO}_3 \cdot \text{CaCO}_3 \cdot 5\text{H}_2\text{O}$ (a *hydrated double carbonate* of sodium and calcium); and *sodium aluminium fluoride*, or *cryolite*, Na_3AlF_6 , occur in various localities. Further details are given below, under the appropriate headings.

Extraction. Sodium has important industrial and technical applications and is consequently manufactured on a considerable scale. The principal method now in use is the electrolysis of a fused mixture of sodium chloride and calcium chloride by the Downs process.

The electrolytic cell is a rectangular iron tank lined with refractory earthenware. The anode, A, is made of graphite, while the cathode, B, shown in section in Fig. 54, consists of an iron cylinder surrounding the anode. An iron-gauze cylinder is placed between the anode and the cathode, to prevent the sodium from wandering into the neighbourhood of the chlorine. The cell contains a fused mixture of 40 per cent of sodium chloride with 60 per cent of calcium chloride. The temperature of the electrolyte ($600-650^{\circ}$) is maintained by the resistance it offers to the current. The molten sodium liberated at the cathode floats to the surface and runs off through the pipe P. The chlorine set free at the anode is used immediately, or collected, liquefied, and stored in cylinders.

An older method, due to CASTNER, is still employed to some extent. It is essentially a large-scale adaptation of Davy's original method of isolating the element, viz. the electrolysis of sodium hydroxide.

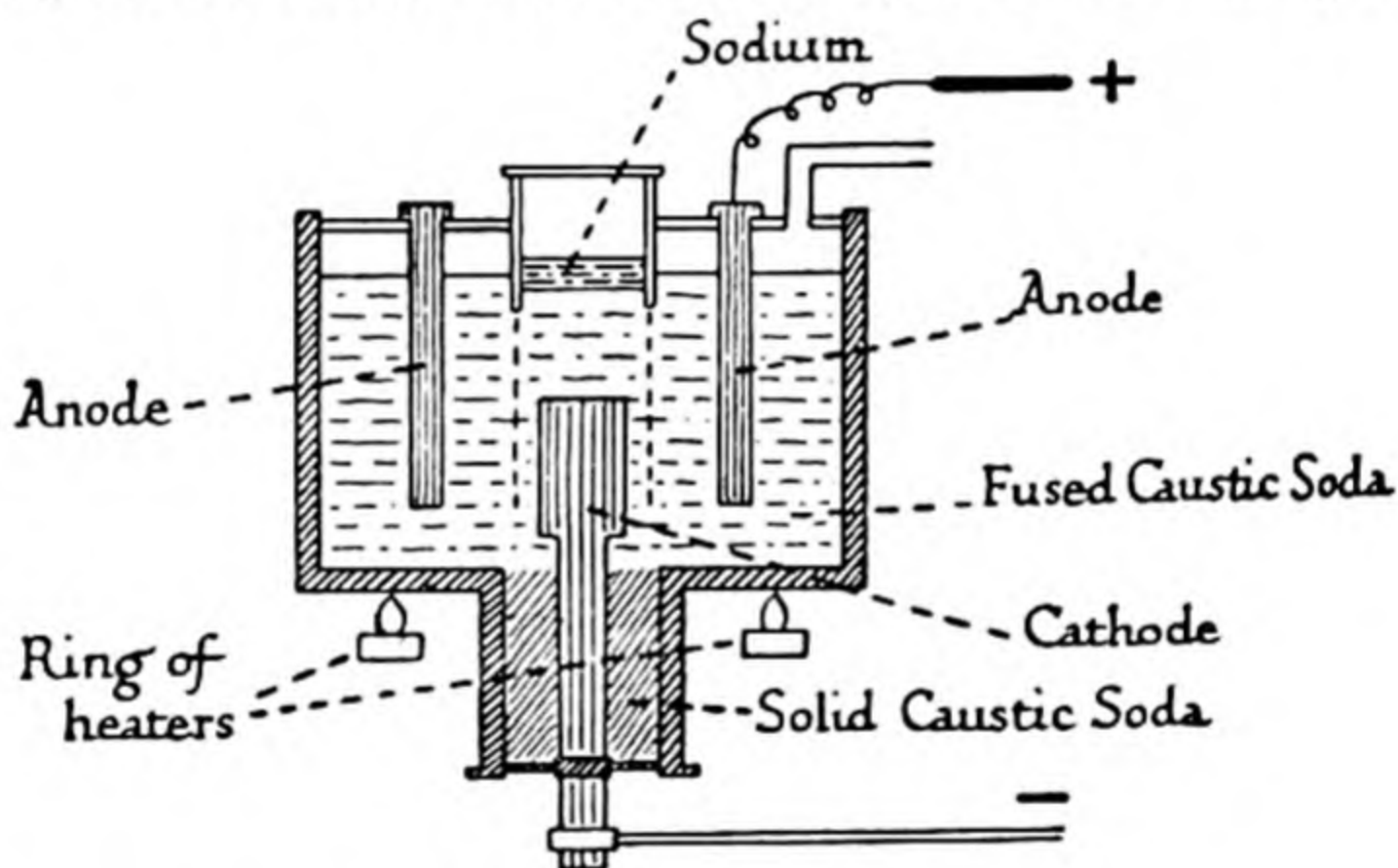


FIG. 55. THE CASTNER CELL

The cell (Fig. 55) is an iron vessel, through the base of which projects the copper cathode, held in position by solidified caustic soda. The anode is a nickel cylinder, and between it and the cathode is a cylinder of steel wire gauze. The cell contains molten caustic soda, which is kept fused (320°) by the heat generated by the current. Oxygen is set free at the anode, and sodium and hydrogen at the cathode. The molten sodium (M.P. 98°) floats to the surface and collects in the cylinder shown in the figure, whence it is removed from time to time.

The business-minded reader will have no difficulty in appraising the rival merits of the two methods. In the CASTNER process, the starting-material has itself to be manufactured. Moreover, the electrolysis

yields (a) oxygen, for which the sale is very small, in nearly as great a weight (16 : 23) as the sodium itself, and (b) hydrogen, which can be prepared much more cheaply in other ways (p. 275). In the Downs process, the by-product is chlorine, which finds a ready sale. The only advantage of the Castner process is its low operating temperature (320°). Calcium chloride acts in the Downs cell only as a solvent, since at 600° its decomposition voltage is greater than that of sodium chloride (p. 247).

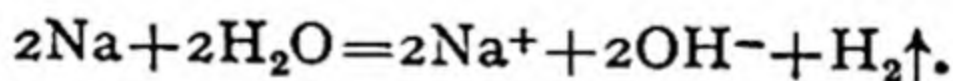
Properties. Sodium is a soft, silvery-white metal of specific gravity 0.97; it melts at 97.5°, and boils at 880° to a violet monatomic vapour. It is an excellent conductor of heat and electricity.

Sodium is unaffected by dry air at ordinary temperatures, but rapidly tarnishes in moist air, since it becomes covered with a film of *sodium monoxide*, Na₂O. This in turn absorbs moisture and forms *sodium hydroxide*, NaOH, which is itself slowly converted into *sodium carbonate*, Na₂CO₃, by the atmospheric carbon dioxide. Sodium is preserved in air-tight drums.

When sodium is heated in air or oxygen, it burns with a brilliant golden-yellow flame, showing the well-known D lines in its spectrum. The product is mainly *sodium peroxide*, Na₂O₂, though a little of the monoxide may be present as well.

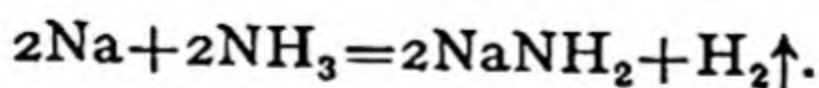
On heating, sodium combines directly with the halogens, phosphorus and sulphur, forming *sodium halides* (NaF, NaCl, NaBr, NaI), *sodium phosphide*, Na₃P, and *sodium sulphides*, e.g. Na₂S (p. 521). It will also combine with hydrogen when heated in the gas to about 360°–380°, forming *sodium hydride*, NaH. It is a strong reducing agent, and if heated with the chlorides or oxides of less electropositive metals will often reduce them to metal.

When placed upon water, sodium floats, but immediately attacks the water to form *sodium hydroxide*, which dissolves, and hydrogen, which escapes:



The heat of the reaction is sufficient to melt the sodium, but not to ignite the hydrogen unless the water is warm or unless the wandering of the sodium is prevented (e.g. by putting it on a piece of floating filter-paper).

If heated in gaseous ammonia, sodium displaces hydrogen and gives *sodamide*, NaNH₂:



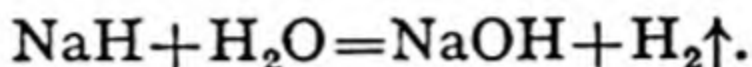
Sodium never forms part of an *anion*.

For *sodium amalgam* see p. 364.

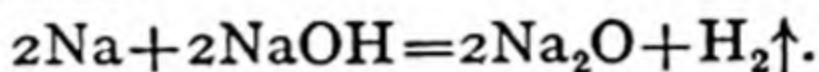
Uses. Sodium is used in the manufacture of *sodium peroxide*, *sodium cyanide*, and *sodamide*, as a synthetic reagent in many organic preparations, and in sodium lamps.

COMPOUNDS OF SODIUM

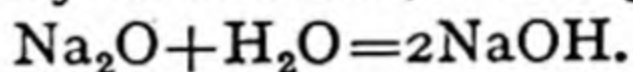
Sodium hydride, NaH , the preparation of which was described on p. 287, is an unstable white crystalline solid which is hydrolysed by water:



Sodium monoxide, Na_2O , is a white solid prepared by fusing sodium with sodium hydroxide:

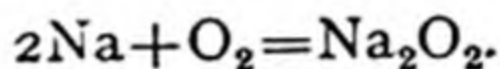


It combines energetically with water, forming the hydroxide:



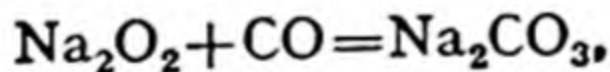
Chemically it behaves as a normal basic oxide.

Sodium peroxide, Na_2O_2 , is obtained when sodium burns in excess of air or oxygen:



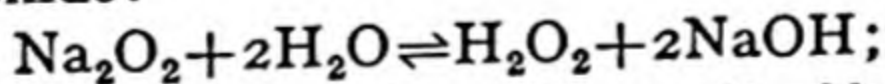
It is manufactured by filling metal trays with sodium, loading the trays on to trucks, and running a train of a dozen laden trucks through an iron tunnel maintained at 300° . A current of air, freed from moisture and carbon dioxide, is blown through the tunnel in the opposite direction. When the train emerges, it is carrying sodium peroxide instead of sodium.

Sodium peroxide is a yellowish powder differing from most peroxides in remaining stable at high temperatures. It is a very vigorous oxidizing agent, converting carbon monoxide to sodium carbonate:



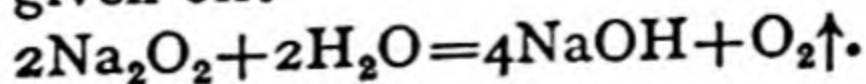
sulphides to sulphates, and ammonia to nitrogen. When brought into contact with hydrogen sulphide, it immediately ignites it. A mixture of sodium peroxide with sugar or paper inflames if moistened.

When sodium peroxide is added to ice-cold water, it is hydrolysed to hydrogen peroxide:

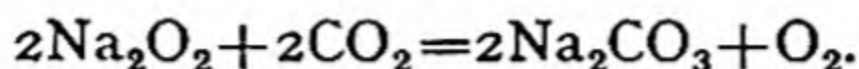


it may, in fact, be regarded as the sodium salt of hydrogen peroxide, which is a weak acid (p. 507).

If water is added to sodium peroxide and the temperature allowed to rise, oxygen is given off:



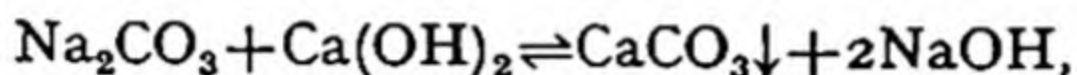
Industrially, sodium peroxide is used as a bleaching-agent, and also as a means of purifying air in confined spaces, e.g. submarines:



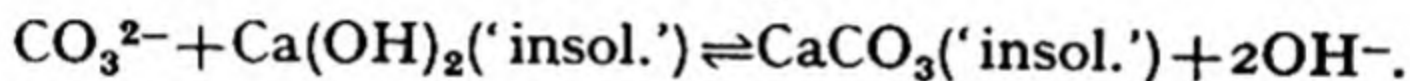
The equation shows that it not only removes carbon dioxide but liberates oxygen.

Sodium hydroxide, caustic soda, NaOH , is manufactured by the GOSSAGE process, from anhydrous sodium carbonate or soda-ash (p. 292), but much is obtained electrolytically as a by-product in the manufacture of chlorine.

Gossage's Method. A 10 per cent solution of sodium carbonate is boiled in a large iron vessel (*causticizer*) by means of a steam-blast. Lumps of fresh quicklime are slaked, and the slaked lime is mixed with water to form milk of lime. The milk of lime is then added to the boiling solution of sodium carbonate, when the reversible change:



takes place, over 90 per cent of the sodium carbonate being converted into the hydroxide. Excess of lime does not give a better yield, since the reaction is essentially:



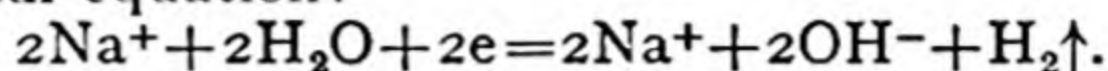
As long as *sufficient* lime is present, therefore, the equilibrium is governed by the relative 'insolubilities' of the $\text{Ca}(\text{OH})_2$ and the CaCO_3 , and since calcium carbonate is very much less soluble than slaked lime, the reaction goes very far to the right.

The solution of sodium hydroxide is filtered off from the sludge of calcium carbonate and remaining lime, and concentrated by evaporation under reduced pressure. On cooling, the unchanged sodium carbonate crystallizes out and is removed. The solution is then completely dehydrated by further heating, and the sodium hydroxide is left in the molten state. It is run off into metal drums, in which it solidifies and which are immediately sealed; or into moulds, where it is cast as sticks or pellets.

The Gossage method, originally worked over a century ago, was for a time largely superseded by the electrolytic method. With the advent of the cheap sodium carbonate of the SOLVAY process, however, it again assumed a prominent position.

Electrolytic Method. In the electrolytic method, which is worked primarily to obtain chlorine, concentrated sodium chloride solution is electrolysed in special cells. Many varieties of these cells are, or have been, used, the main object in all of them being to effect as complete a separation as possible of the sodium hydroxide formed round the cathode from the chlorine set free at the anode.

Except when the cathode is mercury (see below) sodium hydroxide accumulates at the cathode because here hydrogen ion is discharged and leaves hydroxyl ion, OH^- , unpartnered in the solution. The net cathodic reaction may be expressed by the electrochemical equation:



The electrode potential (or discharge potential) of sodium ion is so much more negative than that of hydrogen ion (see p. 244), that the metallic ion cannot be discharged, even when the hydrogen ion is in the very low concentration found in water (p. 217). As explained on p. 39, the anodic product when dilute (less than molar) sodium chloride is electrolysed is *oxygen*, but when the

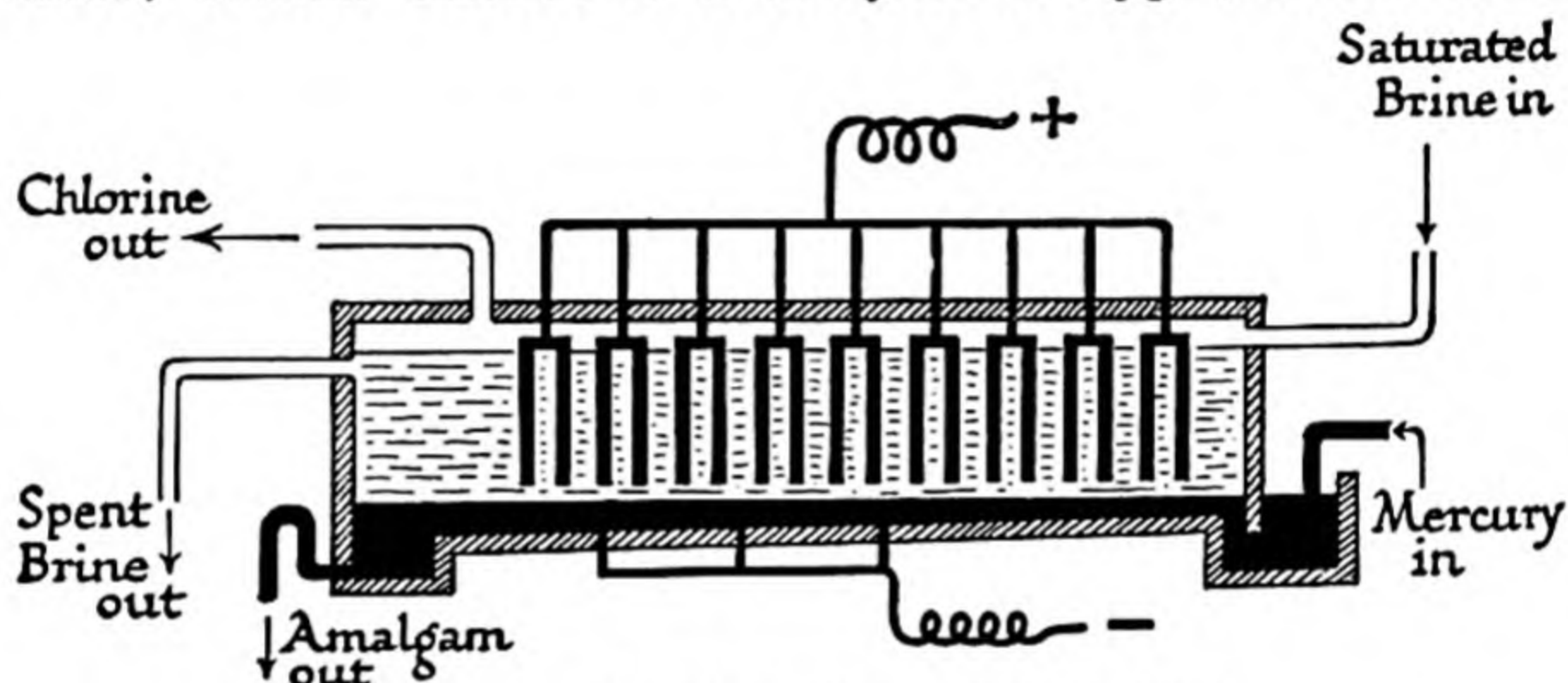


FIG. 56. THE CASTNER-KELLNER CELL

concentration of the chlorine ion is greatly increased, it becomes possible to discharge it in preference to hydroxyl ion.

When mercury is used as cathode the situation is, from the electrochemical standpoint, completely altered. The discharge of sodium ion is made easier (i.e. requires a less negative potential, see p. 247) because sodium dissolves freely in mercury, while the high 'over-voltage' of hydrogen at a mercury electrode (see p. 249) increases the difficulty of discharging hydrogen ion; as the result sodium ion is directly discharged:



Conversely, sodium amalgam reacts only slowly with water, whereas the pure metal acts violently. However, if the hydrogen ion concentration relative to that of the sodium ion is increased, by adding acid, then sodium amalgam is not produced, but hydrogen ion is discharged instead, as at other cathodes.

The CASTNER-KELLNER cell was one of the earliest to be successful and it is still used in a modified form (Fig. 56). Saturated brine is fed

into a large rectangular tank, along the slightly sloping floor of which a stream of mercury flows. The mercury is made the cathode, and a series of carbon plates forms the anode. The voltage used is about 120. On electrolysis, chlorine comes off at the anode, escapes through a pipe (see Fig. 56), and is used directly, or collected, dried, liquefied, and stored. At the cathode, the liberated sodium dissolves in the mercury to form sodium amalgam. This is run off into a lower tank containing water, where the sodium reacts to form sodium hydroxide and hydrogen, and whence the mercury is recirculated through the cell. The hydrogen is collected (generally for direct conversion into hydrogen chloride synthetically), and the solution of sodium hydroxide is evaporated as in the Gossage process. The spent

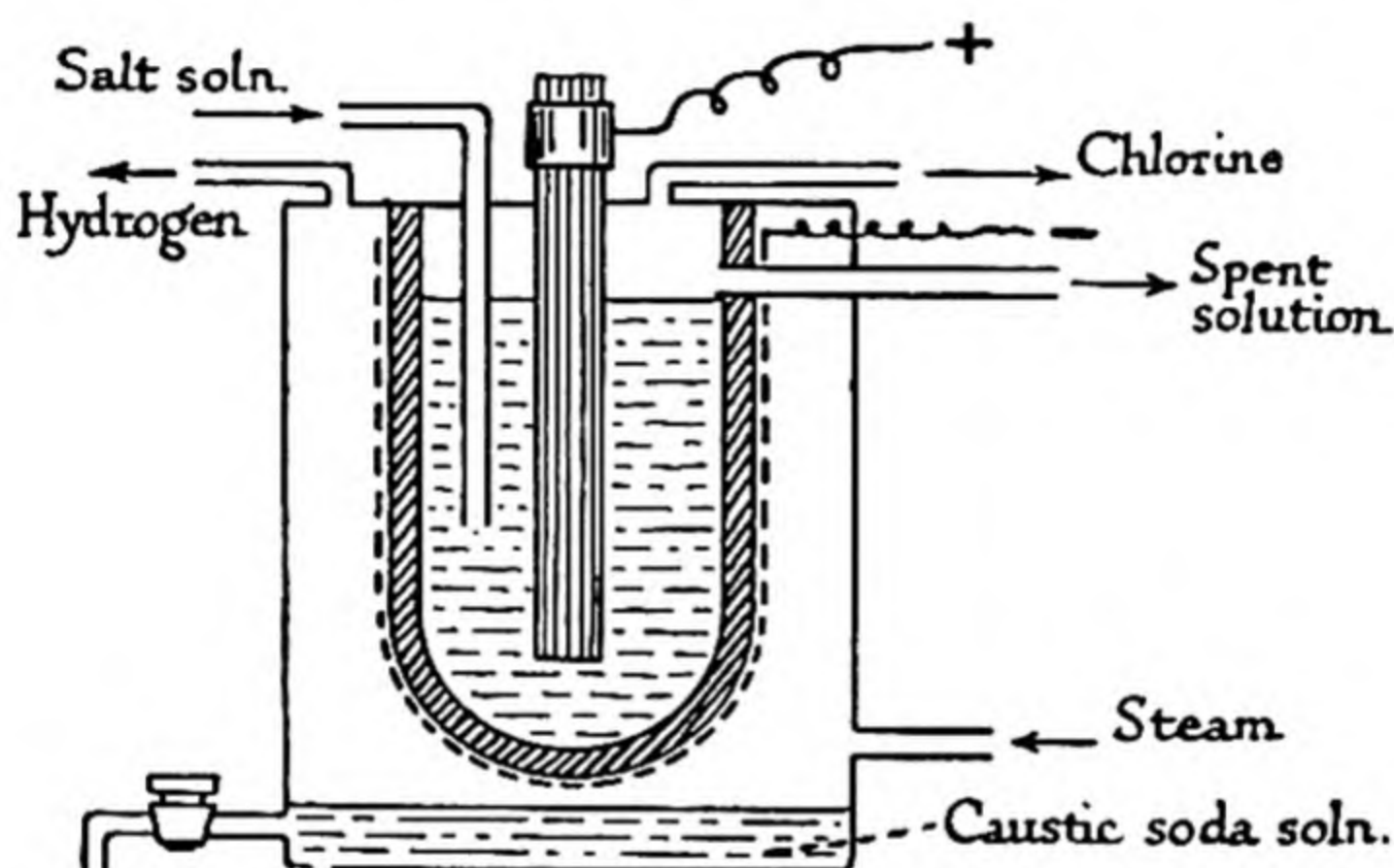


FIG. 57

brine leaving the cell is stirred up with more salt to saturate it again, and is then returned through the pipe shown on the right of the diagram.

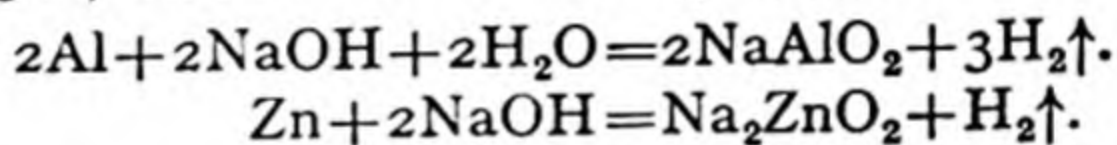
Another type of cell, with a diaphragm (Fig. 57), contains a large trough of asbestos the outer surface of which is covered with perforated iron sheet, forming the cathode. The carbon anode dips into brine, which gradually soaks through the asbestos to the cathode, and electrolysis occurs. A current of steam blown through the outer casing enclosing the cell prevents the accumulation of sodium hydroxide on the cathode, and carries it down as a hot solution. This is run off and evaporated. The hydrogen and chlorine liberated at the cathode and anode respectively are collected and dried, and either combined to form hydrogen chloride or compressed separately into cylinders.

Purification. Commercial sodium hydroxide may contain sodium chloride, carbonate, and sulphate. It may be purified by dissolving it in alcohol and pouring the solution off from the salts, which are practically insoluble. The solution is then evaporated in a silver basin.

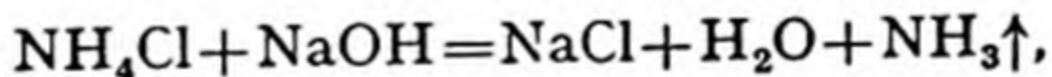
Properties. Sodium hydroxide is a pearly white crystalline solid melting at 318.4° and boiling at about $1,400^{\circ}$. It dissolves readily in water, with considerable evolution of heat. On exposure to air it deliquesces, but the solution gradually resolidifies on absorption of atmospheric carbon dioxide, which converts it into sodium carbonate. (*Contrast* potassium hydroxide, which also deliquesces, but does not solidify again, since potassium carbonate is itself deliquescent.)

The soapy feel of a solution of sodium hydroxide may be partly due to the formation of soap by the action of the hydroxide on oils or fats in the skin. Concentrated solutions quickly dissolve flesh (hence *caustic*, i.e. *burning, soda*).

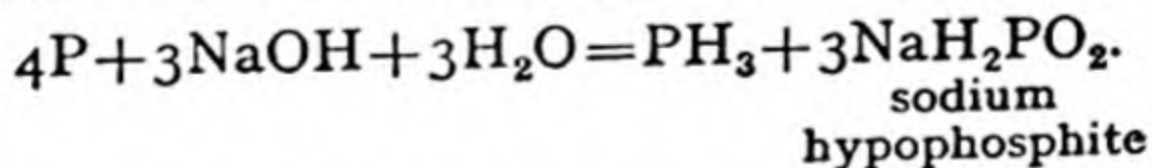
Sodium hydroxide is a very strong base, and precipitates the hydroxides (or oxides) of many metals from solutions containing the metallic ions. In aqueous solution it dissolves metallic aluminium and zinc, with liberation of hydrogen and formation of *sodium aluminate* (p. 380) and *sodium zincate* (p. 357):



When an ammonium salt is heated with sodium hydroxide, ammonia is evolved:



while phosphine, PH_3 , may be prepared by heating yellow phosphorus with concentrated sodium hydroxide solution (p. 464):



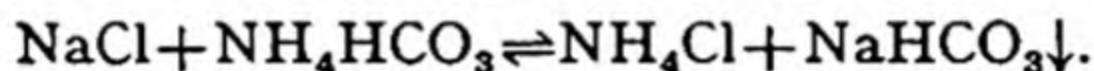
Sodium hydroxide, in solution or fused, gradually dissolves glass as sodium silicate; the concentrated aqueous solution should therefore not be used in burettes, and bottles containing it should be fitted with rubber bungs, not glass stoppers.

In the laboratory, sodium hydroxide is employed as the cheapest strong base, and as an absorbent for carbon dioxide, chlorine, and many other gases. Commercially it is used on a very large scale in making artificial silk, in the conversion of fats into soap, and in the manufacture of other sodium compounds.

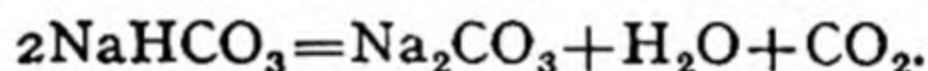
Sodium carbonate, Na_2CO_3 . In the form of its *decahydrate*, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, sodium carbonate is used as washing-soda, but by

far the greater portion is sold as the anhydrous salt, Na_2CO_3 , under the name of 'soda-ash.' Soda-ash has innumerable uses, and it is probably true to say that practically every trade and industry makes use of it at some stage or other. Of the 3,500,000 tons produced every year, about 900,000 tons are used in glass-making. About the same quantity is required in the manufacture of soap, while the textile industry (cotton, linen, etc.) uses about 600,000 tons in normal times. In the manufacture of other chemicals, some 350,000 tons of soda-ash are consumed. The remaining 750,000 tons are used in paper-making and a wide variety of other industries.

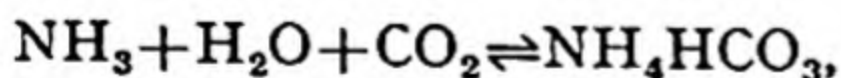
Practically the whole of this vast quantity of soda is produced by the *ammonia-soda* process, sometimes known as the *Solvay* process after its inventor, the Belgian chemist ERNEST SOLVAY (1838–1922). In principle, this process is very simple; it consists in preparing a mixed solution of sodium chloride and ammonium bicarbonate, when sodium bicarbonate, being only slightly soluble, separates out:



The sodium bicarbonate is then heated, when it decomposes into sodium carbonate, water, and carbon dioxide:



The practical stages are as follows. Strong brine is allowed to trickle down a tower in which gaseous ammonia issues from a number of mushroom-shaped baffles; the liquid leaving the tower at the bottom is thus a concentrated solution of sodium chloride and ammonia. This ammoniacal brine is next allowed to flow down a second tower, the 'carbonator,' up which a stream of carbon dioxide is blown. Under these conditions ammonium bicarbonate is formed:



and immediately reacts with the sodium chloride according to the above equation; the reaction is exothermic and the carbonators are therefore cooled by spraying them with water. It should be noted that the reaction is reversible. Under working conditions about three-quarters of the sodium chloride is converted into the bicarbonate.

Strong brine is allowed to

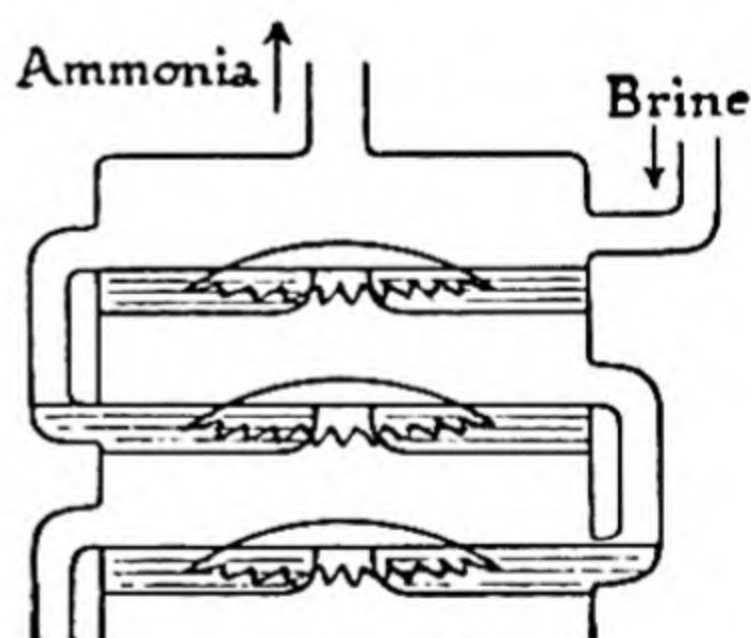


FIG. 58
'MUSHROOM' BAFFLES

The liquid leaving the carbonator contains a sludge of sodium bicarbonate. It is passed on to filters, which are made of flannel stretched on cylindrical frames kept in slow rotation.

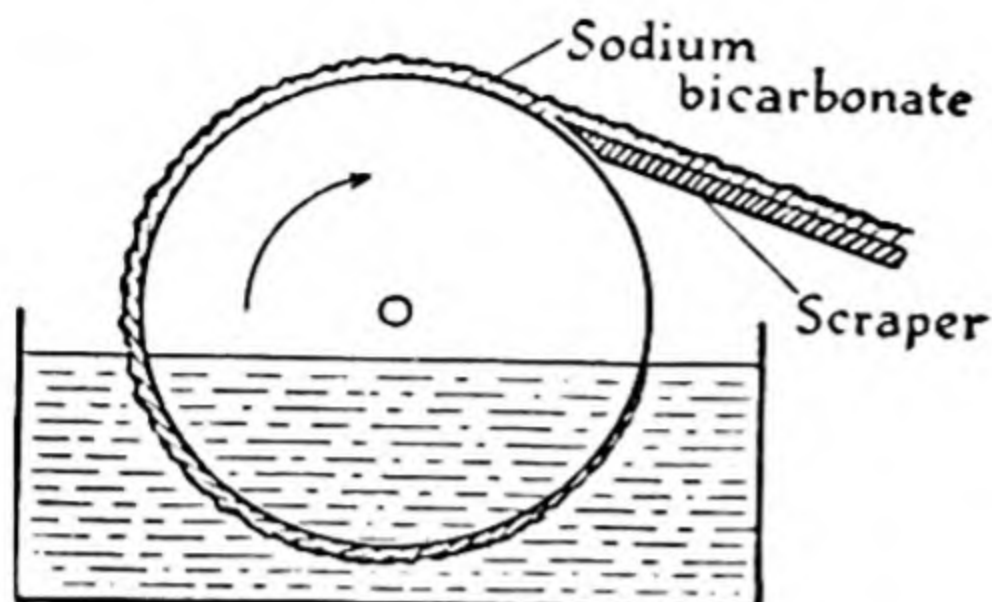
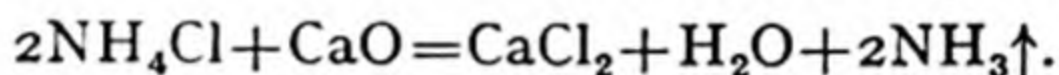


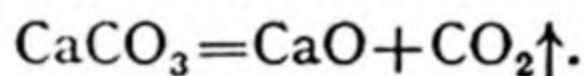
FIG. 59.
FILTER FOR SODIUM BICARBONATE

A vacuum is maintained on the inside of the frames by air-pumps, and the bicarbonate sticks to the flannel, whence it is removed by a scraper. It is then washed with a little water (to remove any ammonium chloride), and heated in suitable furnaces, the carbon dioxide evolved being returned to the carbonators.

The solution of ammonium chloride which leaves the filters is collected and heated with lime; this liberates the ammonia, which is used over again:



The carbon dioxide necessary for the process is obtained by heating limestone in a lime-kiln—a reaction which at the same time provides the lime used to liberate the ammonia from the ammonium chloride:



The other product of the process, calcium chloride, is now also marketable.

The anhydrous sodium carbonate or soda-ash thus prepared is about 99 per cent pure, the chief impurities being sodium chloride and water. Most of it is sold as such, but part is dissolved in water and crystallized out as the decahydrate, 'washing-soda.'

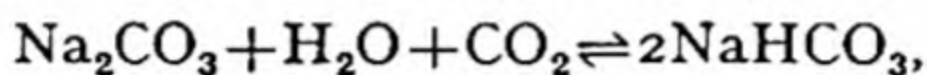
Properties. Anhydrous sodium carbonate is an apparently amorphous white powder, which on exposure to moist air cakes together owing to the formation of hydrates. Several hydrates are known; the commonest is the decahydrate, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, which effloresces in dry air and falls to a white powder consisting of the monohydrate, $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$. When heated, this becomes anhydrous. The anhydrous salt melts at 851° , but is not decomposed by heat.

In aqueous solution, sodium carbonate reacts strongly alkaline. This phenomenon is discussed on p. 229. A corollary of the explanation there given is that free carbonic acid should be present in a solution of sodium carbonate. Carbonic acid, however, is unstable and readily splits up into water and carbon dioxide on heating. On boiling a solution of sodium carbonate, therefore,

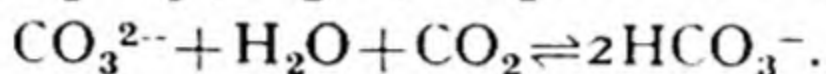
carbon dioxide ought to be evolved if the above explanation is correct; and this deduction is confirmed by experiment, though the rate at which carbon dioxide is lost is slow.

In the laboratory, anhydrous sodium carbonate is used in making up volumetric solutions, and, mixed with potassium carbonate, as 'fusion mixture' in qualitative analysis. The mixture of the two carbonates in equimolecular proportions melts at 690° , while the anhydrous sodium salt melts at 851° and the anhydrous potassium salt at 891° .

Sodium bicarbonate, NaHCO_3 , can be made by passing carbon dioxide into a cold concentrated solution of sodium carbonate, when it separates out as a white crystalline precipitate:



or



It dissolves only moderately in water, the solubility at 0° being 6.9. When the solution is boiled, carbon dioxide is given off and a solution of the normal carbonate is left. A similar dissociation occurs when the solid is heated, which explains why sodium bicarbonate is used in baking ('baking-soda') to make the dough rise.

Sodium sesquicarbonate, $\text{NaHCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$, occurs naturally (mixed with the normal carbonate) in East Africa (Kenya), near Lake Magadi, and also in Utah, U.S.A. Both deposits are very large, and are worked commercially. The African mineral is known locally as *trona* (a corruption of *natron*, p. 284).

For the *estimation of sodium bicarbonate and carbonate*, see p. 232.

Sodium chloride, NaCl . Common salt, the prototype of all salts, occurs in sea-water to the average extent of 2.6–2.8 per cent by weight. Inland seas contain a higher proportion; thus the concentration in the Dead Sea reaches 7.2 per cent, and it has been calculated that this diminutive body of water holds dissolved in it no less than 12,000,000,000 tons of salt. When such inland seas dry up, as sometimes happens, salt-beds are formed. These do not consist of pure sodium chloride, but of all the various salts that were present in the sea-water; sodium chloride, however, usually predominates. Enormous salt-beds exist in many parts of the world, e.g. Wieliczka (near Cracow), Saxony, Utah, the Punjab, and England (Cheshire, Worcestershire). The salt is either mined directly as *rock-salt*, or dissolved in water and pumped up as brine into large pans, where it is obtained by evaporation. In maritime districts it is frequently extracted from sea-water, which is run into shallow ponds and allowed to evaporate by the heat of the sun.

Sodium chloride is an essential article of food. It exists in solution in the blood to the extent of about 2.5 per cent. Roman

soldiers had a ration of salt served out to them regularly; later they received instead a money payment, 'salt-money,' or, in Latin, *salarium*, whence our *salary*.

Sodium chloride is a colourless solid which crystallizes in anhydrous cubes of specific gravity 2.17; it melts at 804° . Its solubility in water varies remarkably little with the temperature, being 35.6 at 0° , 36.3 at 40° , 38.0 at 80° , and 39.8 at 100° . If a solution containing less than 23.6 per cent of salt is cooled sufficiently, pure ice separates out, and the mother-liquor becomes more concentrated. This continues until the concentration reaches 23.6 NaCl per cent, when the solution freezes as a whole at -23° , the eutectic or 'cryohydric' point (p. 141). If a solution containing more than 23.6 per cent of salt is cooled, the solid deposited is salt, and the concentration of the mother-liquor falls until the eutectic point is reached. Therefore -23° represents the lowest temperature that can be obtained with an ice-and-salt freezing-mixture.

Pure sodium chloride is not deliquescent, but the ordinary kitchen variety frequently becomes damp and cakes together in rainy weather, since it contains the deliquescent magnesium chloride as an impurity. Addition of sodium phosphate in appropriate quantity converts the magnesium chloride into magnesium phosphate, which is not deliquescent. The salt therefore loses its tendency to cake, and 'runs' better; at the same time its nutritive value is somewhat increased.

To prepare pure salt, the impure substance is made into a cold saturated solution, and hydrogen chloride is passed in, when pure sodium chloride is precipitated.

Sodium chloride is used as food, as a preservative (e.g. for fish, flesh, and fowl), and as a source of many other substances (e.g. sodium, chlorine, sodium hydroxide, sodium carbonate, and sodium sulphate).

Sodium bromide and **iodide**, NaBr and NaI, resemble the corresponding potassium salts (pp. 305-6).

Sodium chlorate, NaClO_3 , is an important substance manufactured on a large scale by the electrolysis of warm (50°) faintly acid brine containing a small proportion of potassium dichromate. The sodium hydroxide solution formed round the cathode is mechanically swept towards the anode. The following actions then occur:

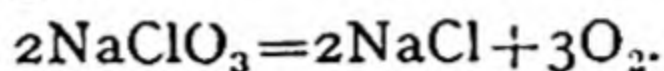
- (i) $\text{Cl}^- + 2\text{OH}^- = \text{ClO}^- + \text{H}_2\text{O} + 2\text{e}^-$.
- (ii) $\text{ClO}^- + \text{H}^+ \rightleftharpoons \text{HClO}$.
- (iii) $2\text{HClO} + \text{ClO}^- = \text{ClO}_3^- + 2\text{H}^+ + 2\text{Cl}^-$.

The actions (ii) and (iii) are purely chemical and occur at all parts of the solution; (i), of course, occurs only at the anode (see also p. 553).

The purpose of the dichromate is to prevent the hydrogen set free at the cathode from reducing the chlorate. Initially, dichromate ion is reduced, by the hydrogen liberated, to an insoluble hydrated oxide of chromium, which forms a continuous film over the cathode, and acts efficiently as a porous partition.

The solution leaving the cell is concentrated, and the very soluble sodium chlorate is separated from the residual sodium chloride by fractional crystallization.

Sodium chlorate is a colourless crystalline solid. When heated, it readily evolves oxygen:



It is an oxidizing agent, and is used in making matches and explosives (e.g. cheddite), and also as a weed-killer.

Much sodium chlorate is converted into potassium chlorate by adding potassium chloride to its concentrated solution. From the liquid, which contains the ions Na^+ , K^+ , ClO_3^- , and Cl^- , the least soluble salt that can be formed from these ions crystallizes out first; this happens to be potassium chlorate.

Sodium nitrate, NaNO_3 . Crude sodium nitrate occurs in immense deposits in the Atacama Desert, or Pampa Salitrera, in the northern part of the South American republic of Chile. The deposits are said to have been discovered 'by a native woodcutter named NEGREIROS, of the Pampa of Tamarugal, by his having made a fire at a certain spot, which still preserves his name, and observing that the ground thereupon began to melt and run like a stream. He hastily reported this fact to his curé at Camiña, who declared it to be hell-fire, and asked to be shown the spot so as to be able to deal with it. The curé took a sample of the salt and found that it was nitre. He threw the remainder into his garden, where, to his surprise, the plants now grew better than before. A British naval officer, visiting Tarapacá some time later, paid a visit to the curé and spread the news to Europe.' *

The nitrate beds—which were first worked commercially by a Bohemian named HAENKE about 1800—are situated at a height of 2,000–5,000 feet above sea-level, and at a distance of some thirty miles from the coast. At least 240,000,000 tons of the mineral are known to exist, and probably still vaster quantities occur in the neighbouring regions not yet adequately explored. The nitrate is found below the surface of the ground at a depth ranging from 2 to 15 feet, and is called *caliche*, or 'Chile saltpetre.' It is covered by a rocky layer, which in turn is covered by a thin bed of sand. Underneath the caliche is a layer of clay.

How the deposits of caliche were formed is not known with

* *Annals of Science*, i. 29 (1936).

certainty. Possibly they represent the final remains of colossal quantities of decaying seaweed, left high and dry by the evaporation of an arm of the sea cut off from the Pacific Ocean by a violent earthquake. This hypothesis is supported by the fact that still recognizable fragments of ancient seaweeds have been discovered in the caliche layers.

In order to mine the caliche, holes are bored down to the layer of clay, and charges of explosive are laid. The explosion breaks up the rock and ore and the caliche is exposed. Gangs of navvies then proceed to crack up the large lumps with pneumatic drills, and the

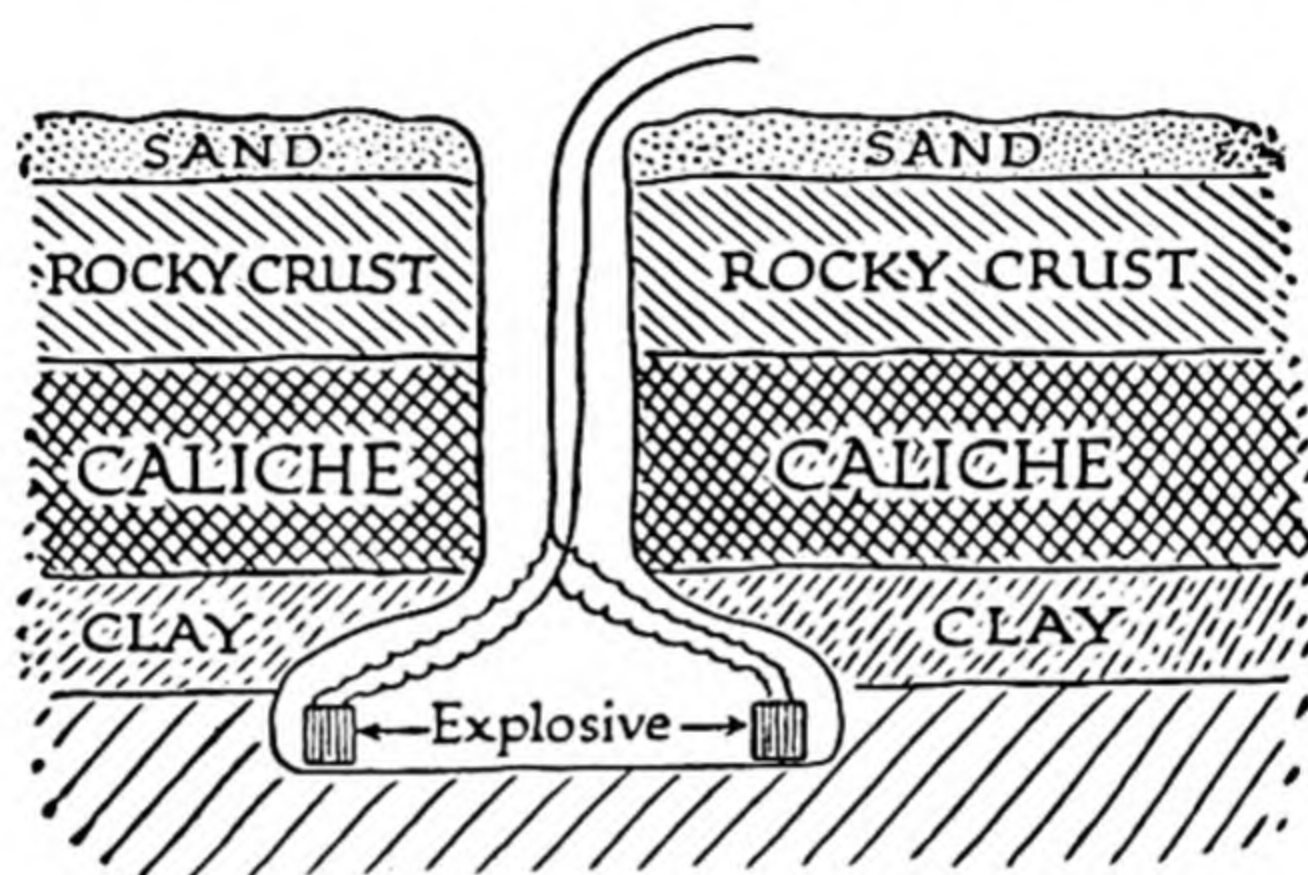


FIG. 60. EXTRACTION OF CALICHE

ore is loaded by mechanical shovels into mule carts, or, if the surface of the ground permits a railway to be built, into a train of trucks. The caliche is transported to the *oficina*, or works, to be refined.

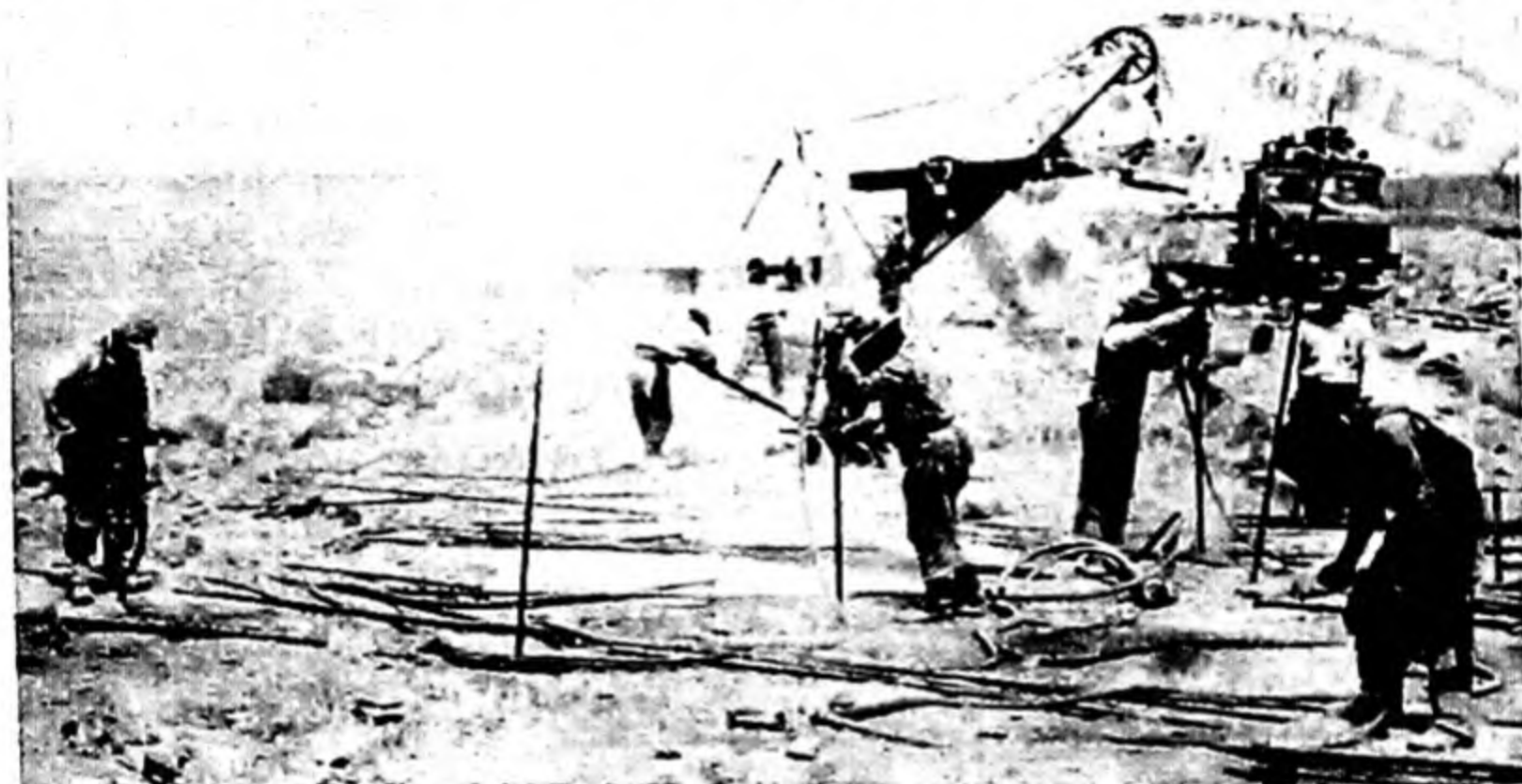
It is first crushed in steam mills, and then dropped into conveyors which carry it to large tanks. Here it is dissolved in hot water, and the insoluble impurities (earth, sand, etc.) are allowed to settle. The clear solution is run off and allowed to cool for four days, during which it deposits most of the nitrate; the mother-liquor is worked up for iodine, which it contains in the form of sodium iodate (p. 563).

The recrystallized nitrate is about 95 per cent pure. It is tipped from the pans on to large sheet-iron drying floors, where it remains for another four days so that any remaining mother-liquor may drain away. It is then dried on cement floors for a further fortnight, after which it is packed ready for shipment into bags holding about 2 cwt. The bags are taken by railway to Iquique and other ports and dispatched to all parts of the world. About four-fifths of the

total quantity produced (which reaches nearly 3,000,000 tons per annum) is applied directly to the soil as a fertilizer (p. 458); some three-quarters of the remainder is used for making nitric acid, and most of the residue for the manufacture of potassium nitrate (p. 307).

Large quantities of sodium nitrate are now manufactured by neutralizing synthetic nitric acid with sodium carbonate.

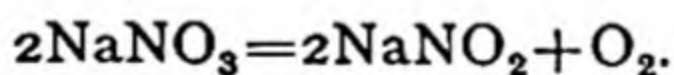
Pure sodium nitrate is a colourless solid crystallizing in rhombohedra which to the casual glance resemble cubes. It is readily soluble in water, its solubility being 73 at 0° and 180 at 100°. Since



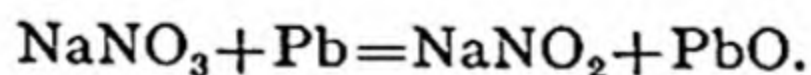
Nitrate Corporation of Chile Ltd.

FIG. 61. MINING CALICHE: DRILLING OPERATIONS BEFORE BLASTING

it is deliquescent it cannot be used as a substitute for the potassium salt in gunpowder. When heated, sodium nitrate melts at 308°, and at a somewhat higher temperature it decomposes into sodium nitrite and oxygen:

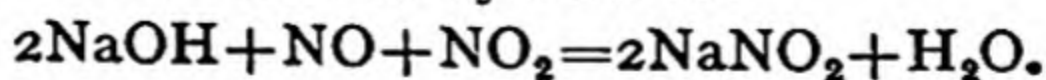


Sodium nitrite, NaNO_2 . Sodium nitrite can be obtained in the way just described, but it is better to fuse the sodium nitrate with lead:



The mass is extracted with water, filtered from lead oxide, and the solution evaporated to the point of crystallization.

An alternative method of preparing sodium nitrite, giving a purer product, is to dissolve nitrous fumes (i.e. a mixture of nitric oxide and nitrogen dioxide made by heating nitric acid with arsenious oxide) in a solution of sodium hydroxide:



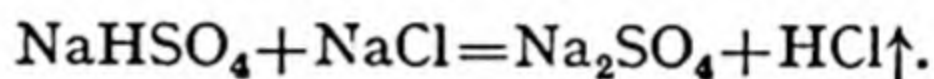
Sodium nitrite is a yellowish crystalline solid, M.P. 271° . It readily dissolves in water to give a slightly yellow solution, which is neutral if the nitrite is pure, but is frequently somewhat alkaline owing to the presence in the nitrite of sodium hydroxide as impurity.

On addition of a dilute acid to a solution of sodium nitrite, oxides of nitrogen are evolved. No doubt nitrous acid is first formed, but this immediately decomposes. The blue colour assumed by the solution is due to the presence of nitrous anhydride, N_2O_3 . If the acidified solution is rapidly shaken with benzene, all the blue colour passes into the benzene layer.

Sodium nitrite is largely used in the dye industry, since if it is added to a cold acidified solution of a primary aromatic amine (e.g. aniline, $C_6H_5.NH_2$) it yields reactive compounds (*diazonium salts*) which are the parent substances of innumerable colouring-matters—the so-called ‘azo-dyes.’

For the structure of the nitrite ion, see p. 446.

Sodium sulphate, Na_2SO_4 . Anhydrous sodium sulphate is obtained on the large scale by heating sodium hydrogen sulphate (q.v.) with sodium chloride in a reverberatory furnace:

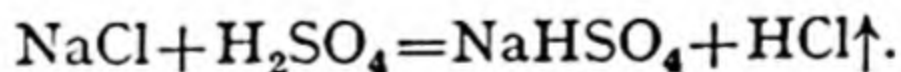


It is a colourless solid with sufficient affinity for water to render it useful as a drying agent in organic chemistry, in those cases where the ordinary drying agents are unsuitable. It dissolves readily in water, from which it crystallizes as the decahydrate, $Na_2SO_4 \cdot 10H_2O$ (GLAUBER'S salt). Crystals of the decahydrate are efflorescent in dry air, falling to a powder of the anhydrous salt. On heating, they melt at 32.4° and decompose, depositing some of the anhydrous sulphate.

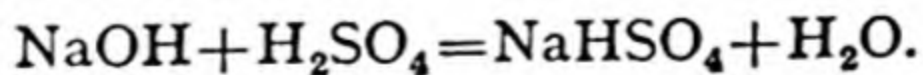
Sodium sulphate is used in glass-making, and as a source of sodium sulphide. The decahydrate is used as a purge.

For the *solubility curve* of sodium sulphate, see p. 139.

Sodium hydrogen sulphate, sodium bisulphate, $NaHSO_4$, is obtained when sodium chloride is gently heated with concentrated sulphuric acid:

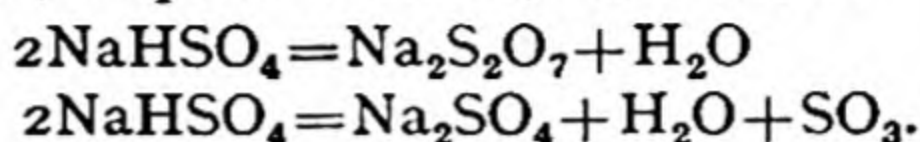


It may also be prepared by adding dilute sulphuric acid to sodium hydroxide solution in the correct proportions, and evaporating the solution to crystallization:

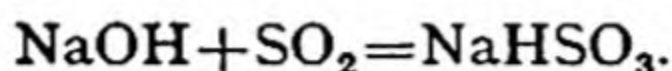


Sodium bisulphate is a colourless crystalline solid which dissolves in water to give the ions Na^+ , H^+ , and SO_4^{2-} ; it may therefore often be employed in place of sulphuric acid. When heated carefully it

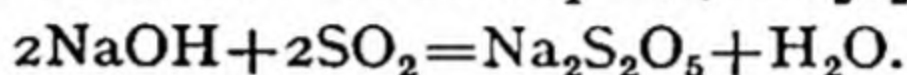
yields *sodium pyrosulphate*, $\text{Na}_2\text{S}_2\text{O}_7$, but at a red heat it decomposes into sodium sulphate, sulphur trioxide, and water:



Sodium sulphite, Na_2SO_3 . When sodium hydroxide solution is saturated with sulphur dioxide, the main product is *sodium bisulphite*, NaHSO_3 :

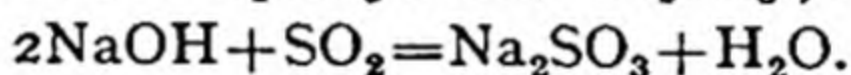


If, however, the solution is very concentrated, and kept cold, colourless crystals of *sodium 'metabisulphite'*, $\text{Na}_2\text{S}_2\text{O}_5$, may separate:



This salt is used in photography.

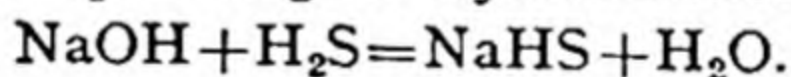
To prepare *sodium sulphite*, sulphur dioxide is passed into sodium hydroxide solution until the solution is neutral, or only faintly alkaline. On evaporation, the sulphite separates in the form of colourless crystals of the *heptahydrate*, $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$:



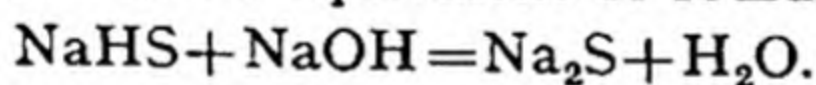
For the general properties of sulphites, see p. 527.

Sodium thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3$. See p. 536.

Sodium sulphide, Na_2S , and **sodium hydrosulphide**, NaHS . When a solution of sodium hydroxide is saturated with hydrogen sulphide, sodium hydrosulphide is formed, and can be obtained in the form of its *dihydrate* by evaporating to crystallization:

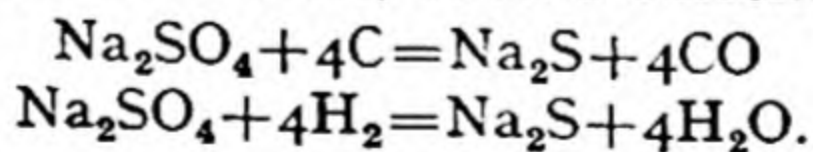


From a solution of the hydrosulphide, the sulphide may be prepared by addition of an equivalent of sodium hydroxide:



On evaporation, colourless crystals of the *enneahydrate*, $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, are formed.

Commercially sodium sulphide is obtained by strongly heating sodium sulphate with anthracite, or in a current of hydrogen:



The mass resulting from reduction with anthracite is steeped in water, and after filtration from insoluble matter the solution is evaporated to give crystals of the hydrated sulphide. Sodium sulphide is used industrially in the dye industry and in tanning.

When sodium sulphide is heated with sulphur, a yellow substance known as *sodium polysulphide* is obtained. This is probably a mixture, varying in composition from Na_2S_2 to Na_2S_5 .

Tests for Sodium.

1. Flame: strong, persistent, golden-yellow colour.
2. Solutions of sodium salts give with
 - (a) potassium 'pyro-antimonate': white precipitate of sodium 'pyro-antimonate,' $\text{NaSb}(\text{OH})_6 \cdot \text{H}_2\text{O}$, slightly soluble in boiling water;
 - (b) zinc uranyl acetate in dilute acetic acid: yellow crystalline precipitate of sodium zinc uranyl acetate,
$$\text{NaZn}(\text{UO}_2)_3(\text{CH}_3\text{COO})_9 \cdot 9\text{H}_2\text{O}.$$

POTASSIUM, K

Atomic number: 19. *Atomic weight:* 39.100. *Specific gravity:* 0.85. *Melting-point:* 64°. *Boiling-point:* 760°.

History. Potassium carbonate occurs in wood-ash, from which it was extracted with water. The solution was evaporated in iron pots, yielding a white solid known as pot-ash. The word *potassium* was coined by adding the suffix *-ium* (indicating a metal) to *potash*, and toning down the slight air of insobriety attaching to 'potashium' by elision of the *h*. Metallic potassium was first prepared by SIR HUMPHRY DAVY in 1807 (see p. 285).

Occurrence. Potassium compounds are widely distributed. The sea contains about 1 per cent of potassium chloride, and the saline deposits formed by the evaporation of inland seas are rich in potassium salts. At Stassfurt, for example, the salt-beds contain large quantities of *sylvine*, KCl , *carnallite*, $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, and *kainite*, $\text{KCl} \cdot \text{MgSO}_4 \cdot 3\text{H}_2\text{O}$. Similar deposits of potassium salts occur in Alsace, United States, Russia, Palestine (Dead Sea), and other regions. *Potassium aluminium silicate* or *felspar*, KAlSi_3O_8 (or $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$), is a common rock, from which, by weathering, potassium compounds pass into the soil and thence into plants. Intensive agriculture seriously depletes the soil supply of potassium salts, which are essential to plant life, and it is therefore necessary to dress cultivated soils with 'potash fertilizers' such as kainite.

Extraction. Metallic potassium is manufactured by the electrolysis of the fused hydroxide, though owing to technical difficulties—such as the fact that potassium dissolves in fused potassium hydroxide—the electrolysis of the fused chloride is now more generally preferred.

Properties. In both its physical and its chemical properties, potassium closely resembles sodium. It is a soft white metal melting at 64°, and boiling at 760° to give a beautiful green mon-atomic vapour. Its specific gravity is 0.85, so that it floats on water. Like sodium, it is a good conductor of heat and electricity. Unlike sodium it is slightly radioactive, owing to the presence of the isotope $^{40}_{19}\text{K}$ in minute amounts.

Potassium is distinctly more reactive than sodium, but the course of its reactions is usually the same. An exception to the rule is its behaviour on combustion, when it yields a deep yellow superoxide KO_2 and not a peroxide K_2O_2 .

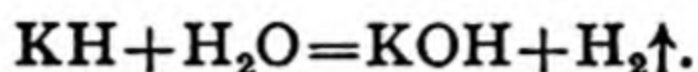
The heat of its reaction with water is sufficient to raise the temperature of the hydrogen to ignition point; the gas burns with a lilac flame characteristic of the presence of potassium compounds.

It is of interest that, while potassium salts are closely similar to

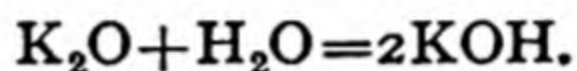
sodium salts in their chemical properties, they often differ widely in their physiological properties. For example, potassium chloride may not be substituted for sodium chloride as an article of diet.

COMPOUNDS OF POTASSIUM

Potassium hydride, KH , is a colourless unstable solid made synthetically by heating potassium in hydrogen. It is hydrolysed by water:



Potassium monoxide, K_2O , is made by the oxidation of potassium in liquid ammonia, or by carefully heating potassium in a supply of oxygen insufficient to form the superoxide. It is a white or yellowish-white solid which combines with water to form the hydroxide:



Potassium superoxide, KO_2 , is a yellow solid made by burning potassium in air or oxygen. It reacts with cold water with evolution of oxygen and formation of hydrogen peroxide:



Potassium superoxide is an even stronger oxidizing agent than sodium peroxide, converting carbon monoxide to carbon dioxide at the temperature of boiling water.

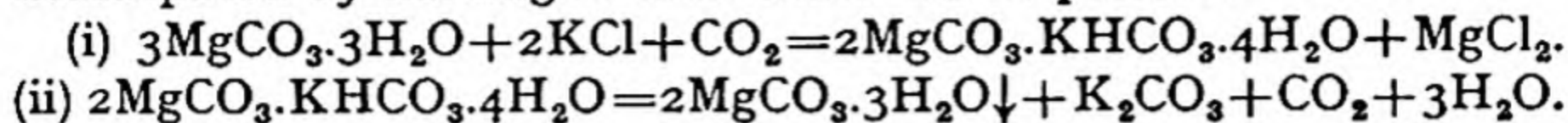
Potassium hydroxide, caustic potash, KOH , is so similar to sodium hydroxide (q.v.) that no account of its chemical properties need be given. However, whereas solid sodium hydroxide contains at least 95 per cent NaOH , solid potassium hydroxide usually contains not more than 80 per cent KOH , the remainder being water. It is rather more hygroscopic than sodium hydroxide and is therefore more commonly used as a drying agent in organic chemistry. It also dissolves more freely in water and in alcohol. M.P. 360° .

Commercially it is used in making *soft soap*, which consists of a mixture of potassium oleate, stearate, and palmitate with a certain amount of glycerol and water.

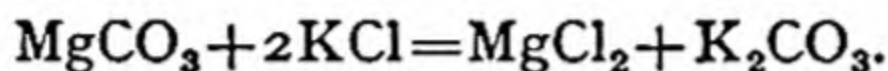
Potassium carbonate, pearl-ash, potash, K_2CO_3 , is a colourless deliquescent solid, M.P. 891° , which crystallizes from aqueous solution as the *dihydrate*, $\text{K}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$. It is extremely soluble in water and the solution is strongly alkaline.

Potassium carbonate cannot be made by the Solvay process (p. 293), since the solubility of potassium bicarbonate is too great. It is therefore manufactured by PRECHT's process, which consists in passing carbon dioxide through a suspension of hydrated magnesium carbonate in a concentrated solution of potassium chloride. The white precipitate of hydrated magnesium potassium hydrogen

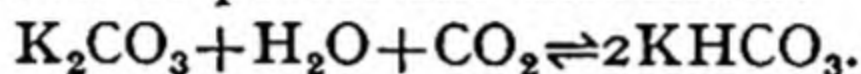
carbonate so formed is separated from the mother-liquor and decomposed by heating it with water under pressure:



The hydrated magnesium carbonate is filtered off and used again, while the filtrate is evaporated to dryness, yielding anhydrous potassium carbonate. It will be observed that the net change in the process is:



Potassium bicarbonate, KHCO_3 , is obtained as a colourless crystalline precipitate when carbon dioxide is passed into a cold concentrated solution of potassium carbonate:



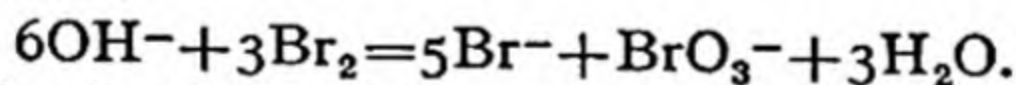
Its solubility in cold water (22.4) is more than three times as great as that of sodium bicarbonate (6.9), so that, under the conditions of the Solvay process, it remains dissolved.

On heating, it decomposes readily into the normal carbonate, water, and carbon dioxide.

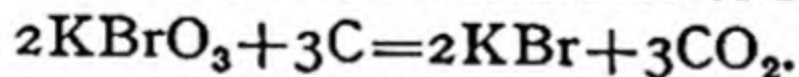
Potassium chloride, KCl , occurs naturally as *sylvine*, and the supply is augmented by extracting it from *carnallite*, $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. The carnallite is mixed with a little water, when the magnesium chloride dissolves and a pasty mass of solid potassium chloride is left. This is purified by recrystallization.

Unlike sodium chloride, potassium chloride is much more soluble in hot water than in cold water (28 at 0° , 34.7 at 20° , 56.7 at 100°).

Potassium bromide, KBr , is made in this country by the action of bromine (from Palestine, see p. 557) on concentrated potassium hydroxide solution:

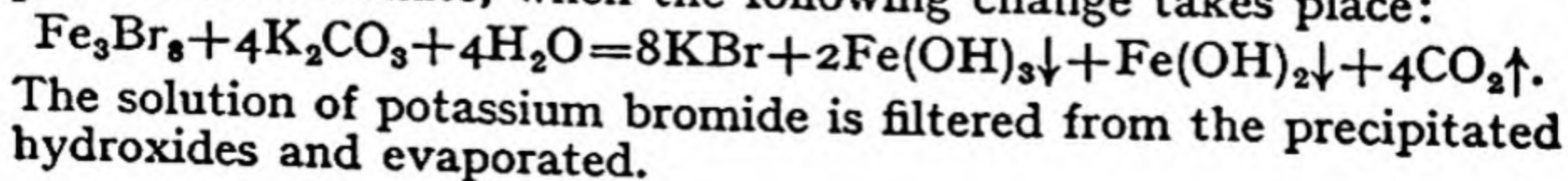


The solution of mixed bromide and bromate is evaporated to dryness, and the residue is heated with charcoal to reduce the bromate:



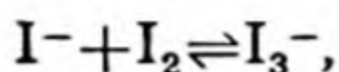
The solution obtained on addition of water is filtered free from excess of charcoal, and evaporated to dryness, when cubic crystals of potassium bromide are left.

Potassium bromide is also prepared from the iron bromide, Fe_3Br_8 , obtained in the manufacture of bromine (p. 556). The iron bromide solution is mixed with the calculated quantity of potassium carbonate, when the following change takes place:



Potassium bromide is used in medicine as a sedative and sleeping-draught, but its habitual consumption impairs the mental powers. In photography, potassium bromide is employed as a restrainer in development, and also in making silver bromide for the sensitive film.

Potassium iodide, KI, is prepared by methods similar to those used to prepare the bromide, which it resembles in crystalline structure and chemical properties. It is readily soluble in water, and the solution is a good solvent for iodine. JAKOWKIN has shown that a solution of iodine in potassium iodide contains the complex ion I_3^- , and the compound $KI_3 \cdot H_2O$ has actually been isolated as black crystals. The reaction:



is reversible, so that all the iodine which has been dissolved in a solution of potassium iodide may be titrated as free iodine with sodium thiosulphate.

Potassium iodide solution also dissolves cadmium iodide and mercuric iodide, to form the complex anions CdI_4^{2-} (p. 207) and HgI_4^{2-} (p. 368).

Potassium chlorate, $KClO_3$, is manufactured by mixing concentrated solutions of sodium chlorate (p. 297) and potassium chloride. The liquid then contains the ions Na^+ , K^+ , Cl^- , and ClO_3^- , and the comparatively small solubility product of $[K^+]$ and $[ClO_3^-]$ is exceeded, so that crystals of potassium chlorate separate out.

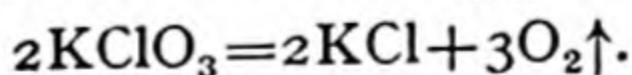
Potassium chlorate is a colourless anhydrous crystalline solid, slightly soluble in cold water (71 gm./litre at 20°), but more readily in hot water (570 gm./litre at 100°). When heated, it melts to a colourless liquid at 370° ; slightly above this point, however, the liquid resolidifies, owing to the formation of *potassium perchlorate*:



On further heating, the perchlorate itself melts, and decomposes into potassium chloride and oxygen:

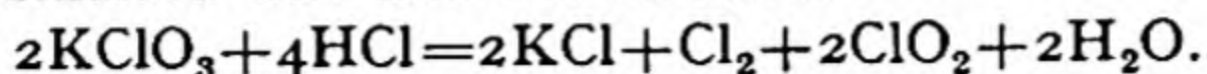


If mixed with manganese dioxide (or certain other catalysts, such as ferric oxide) potassium chlorate decomposes, into potassium chloride and oxygen, below the melting-point:

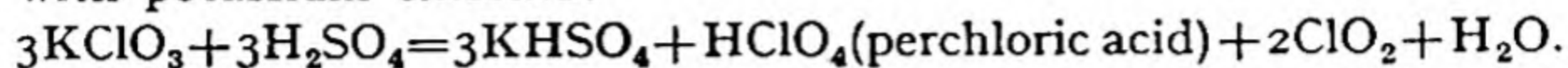


Potassium chlorate is a powerful oxidizing agent, mixtures of it with phosphorus or sulphur being dangerously explosive and liable to explode on slight friction. It oxidizes ferrous salts in acid solution to ferric salts, sulphurous acid to sulphuric acid, and manganates to permanganates.

When warmed with concentrated hydrochloric acid it yields a mixture of chlorine and chlorine dioxide:



Concentrated sulphuric acid also yields chlorine dioxide (p. 551) with potassium chlorate:



(This is an exceedingly dangerous reaction, chlorine dioxide being violently explosive. It should not be carried out with more than the minutest quantity of material.)

Potassium chlorate is used to some extent medicinally as a germicide, but its main industrial application is as an oxidizing agent in the manufacture of matches, fireworks, and explosives.

Potassium perchlorate, KClO_4 , prepared by heating the chlorate to 370° – 380° , can be extracted from the cooled mass by fractional crystallization from water. Industrially it is obtained by the electrolysis of cold concentrated sodium chlorate solution, followed by precipitation with potassium chloride. The perchlorate may be freed from chlorate by digesting with concentrated hydrochloric acid, with which the perchlorate has no action.

Potassium perchlorate is a colourless crystalline solid only slightly soluble in water (7.5 gm./litre at 0°), and insoluble in alcohol and ether. Its formation is used as a test for potassium in presence of sodium (ammonium perchlorate, though much more soluble than the potassium salt, is still only 'slightly soluble,' hence ammonium should be removed before the test is applied).

Contrary to expectation, the perchlorate has only extremely feeble oxidizing powers, as shown by the method of purification mentioned above: even on acidification, the salt does not oxidize potassium iodide in aqueous solution. Its crystals are isomorphous with those of potassium permanganate.

Potassium nitrate, KNO_3 , is popularly known as *nitre* or (Indian) *saltpetre*.* It occurs in the soil of tropical countries, where it is formed by bacterial oxidation of nitrogenous organic material in the presence of the potassium salts in the soil. It was formerly obtained on a large scale by leaching it out of the soil with water, but this method is now of mere local importance.

The modern method of manufacturing potassium nitrate is to mix hot saturated solutions of potassium chloride and sodium nitrate. From the mixed solution, which contains the ions Na^+ , K^+ , Cl^- , and NO_3^- , the least soluble salt will separate first, on evaporation. Of the possible combinations, viz. NaCl , KCl , NaNO_3 , KNO_3 , sodium chloride is least soluble in the hot solution, and, by

* i.e. literally 'rock-salt'—a reminder that in bygone days chemists found it very difficult to distinguish between substances of similar appearance.

concentrating the solution to a specific gravity of about 1.5, nearly all the sodium crystallizes out in this form. The sodium chloride is removed, and the residual solution cooled to about 15°, at which temperature potassium nitrate is the least soluble salt and therefore separates. Purification is effected by recrystallization.

Potassium nitrate is a colourless crystalline solid, which melts at

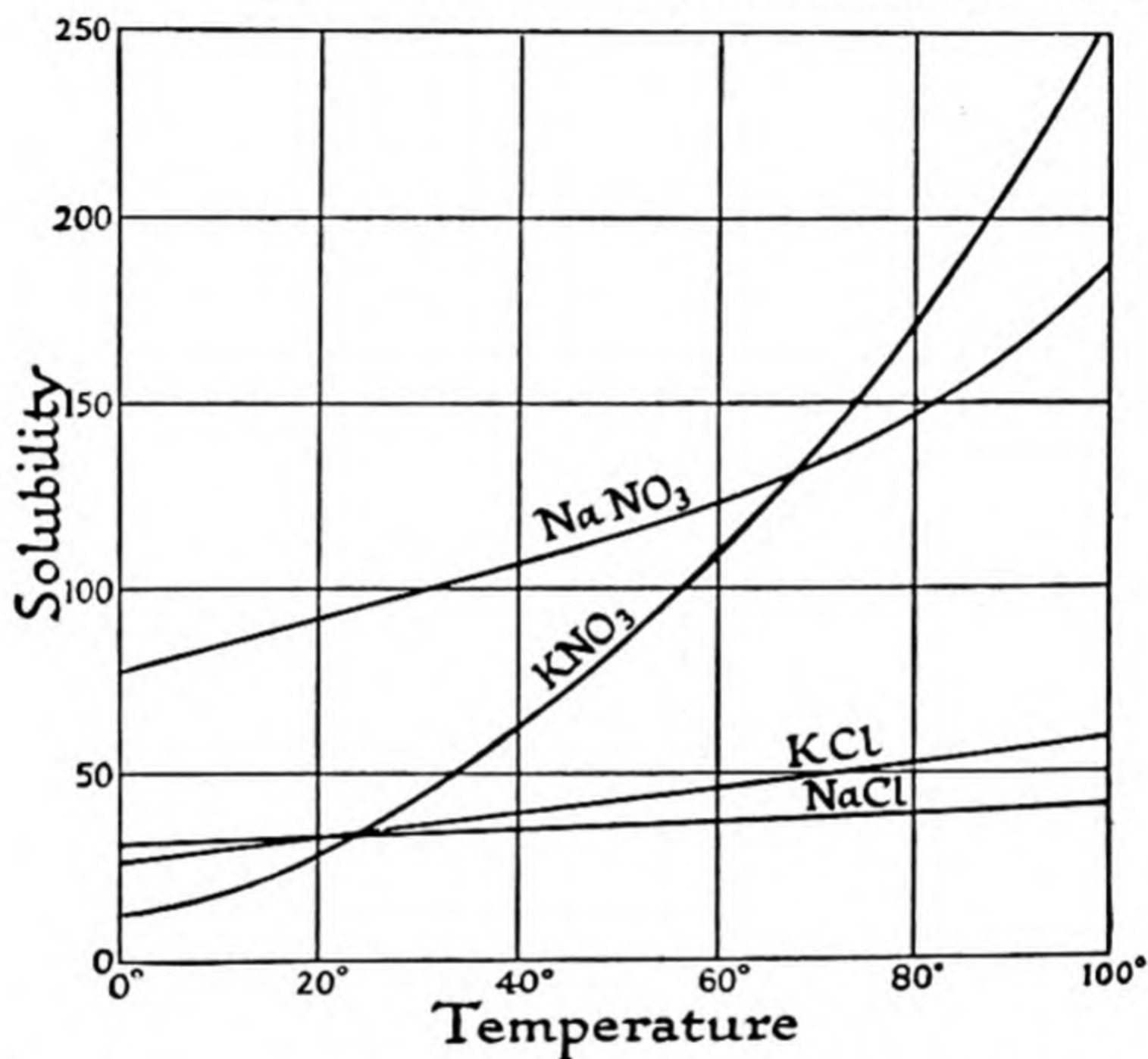
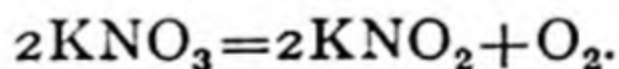


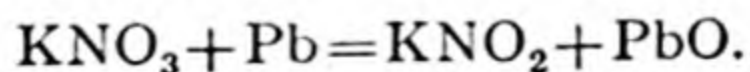
FIG. 62. SOLUBILITY RELATIONSHIPS OF NaCl, KCl, NaNO₃, KNO₃

334° and decomposes at a higher temperature into potassium nitrite and oxygen:



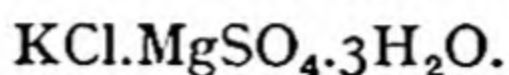
In its general properties it resembles sodium nitrate, but is not deliquescent; it is therefore suitable for use as the oxidizing agent in gunpowder (KNO₃, 75 per cent; C, 15 per cent; S, 10 per cent—slight variations are made according to the purpose for which the powder is required).

Potassium nitrite, KNO₂, is a yellowish crystalline solid made by heating the nitrate alone, or, preferably, with lead as a reducing agent:



It is deliquescent and very soluble in water.

Potassium sulphate, K_2SO_4 , can be made by any of the usual methods, but is obtained commercially from kainite,



The kainite is dissolved in hot water and the solution allowed to cool, when crystals of the double salt *schoenite* separate out, and magnesium chloride remains in the mother-liquor. The *schoenite*, $K_2SO_4.MgSO_4.6H_2O$, is re-dissolved in hot water, and two G.F.W. proportions of potassium chloride (*sylvine*) are stirred into it. The solution thus contains the ions K^+ , Mg^{2+} , SO_4^{2-} , and Cl^- , and on cooling deposits the least soluble salt which can be formed from these ions, viz. potassium sulphate.

Potassium sulphate forms colourless *anhydrous* crystals and is not nearly so soluble as sodium sulphate (its solubility at 0° is only 6.9). It is used as a fertilizer, especially for potatoes, sugar-beet, and tobacco.

Potassium bisulphate, $KHSO_4$, is closely similar to sodium bisulphate.

Potassium sulphide, K_2S , can be prepared by heating the sulphate in a current of hydrogen. *Liver of sulphur* is a mixture of potassium polysulphides, K_2S_x , potassium sulphate, potassium thiosulphate, and sulphur, made by fusing sulphur with pearl-ash (K_2CO_3); to the vivid imagination it resembles liver in appearance. It is used by gardeners for making a wash to destroy moulds, insects, and other pests, but should not be used near painted woodwork (as in a greenhouse) since it converts the white lead of the paint into black lead sulphide.

For other potassium salts, consult the index.

Tests for Potassium.

1. Flame: lilac.

2. Concentrated solutions of potassium salts give with

- (a) chloroplatinic acid: yellow crystalline precipitate of *potassium chloroplatinate* (platinichloride), K_2PtCl_6 , insoluble in alcohol (*note* that potassium iodide does not give this precipitate, since soluble K_2PtI_6 is formed);
- (b) tartaric acid: colourless crystalline precipitate of *potassium hydrogen tartrate*, $KHC_4H_4O_6$;
- (c) sodium perchlorate: colourless crystalline precipitate of *potassium perchlorate*, $KClO_4$;
- (d) sodium cobaltinitrite, $Na_3[Co(NO_2)_6]$, and dilute acetic

acid: yellow precipitate of *potassium sodium cobaltinitrite*, $K_2Na[Co(NO_2)_6]$;

- (c) picric acid: yellow crystalline precipitate of *potassium picrate*, $C_6H_2(NO_2)_3OK$.

N.B. Ammonium gives similar results to potassium in many of these tests, and should therefore be removed before applying them.

COMPARATIVE EXERCISES

1. Draw up a parallel table showing as many as possible of the ways in which sodium and potassium resemble one another. Begin with physical properties (e.g. lustre, hardness, density); then deal with the chemical properties of the elements themselves (e.g. valency, reactions with air, water, halogens); and finally show the resemblance between typical compounds of the two elements.

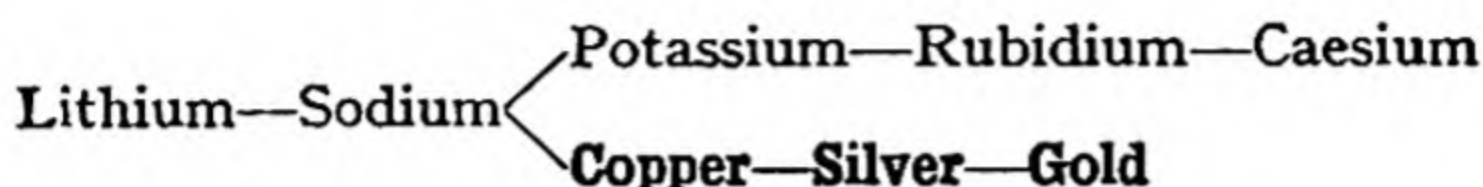
2. Make a list of any differences between sodium and potassium and their chief compounds.

3. Note any resemblances between sodium and hydrogen.

CHAPTER XXIII

GROUP I

COPPER, SILVER, GOLD



The Coinage Metals. Sub-group B consists of the so-called 'coinage metals'—a name appropriate before the introduction of paper money and the substitution of copper-nickel alloys for those of copper-silver. They are all 'noble' metals, falling below hydrogen in the electrochemical series. Towards the alkali metals they have little, if any, resemblance, their nearest analogues being the transitional elements. Unlike the alkali metals, they form complex ions.

COPPER, Cu

Atomic number: 29. *Atomic weight:* 63.54. *Specific gravity:* 8.95.
Melting-point: 1,083°. *Boiling-point:* 2,300°.

History. A common ore of copper, *malachite*,* is not only attractive in appearance, but readily reduced to the metal by heating with carbon. Copper has therefore been known for at least six thousand years, and under the PHARAOHS copper-smelting was a large and important industry. PLINY says that the Romans used to obtain copper from Cyprus, whence the Latin name *cuprum* and, later, our own word *copper*. Alloys of copper have also been in use since very early times. Metallic rosettes excavated at the Roman site at Silchester (Hampshire) were found to consist of *brass* (copper-zinc), while *bronze* (copper-tin) was generally preferred to copper itself on account of its greater hardness and resistance to corrosion. The mastery of their art shown by the ancient metal-workers is well illustrated by the Colossus of Rhodes. This bronze statue of the sun-god, Helios, erected in the third century B.C., was about 30 metres high, and its construction occupied CHARES, the sculptor, nearly twelve years. It cost £200,000—an enormous sum of money in those days—and when it was broken up and sold as

* So called because its green colour resembles that of the mallow (Greek, *malachē*).

scrap to the Saracens in A.D. 653, no fewer than 900 camels were required for the transport.

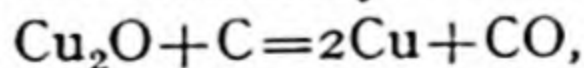
Occurrence. Native copper occurs in many districts, particularly near the Great Lakes in North America, where boulders weighing over 400 tons have been discovered. In small quantities, copper compounds are very widely distributed in nature; thus they occur in most soils and foodstuffs, in seaweed, in the blood of the cuttlefish, in the red colouring-matter of the plumage of the turacou and certain other birds, and in the human liver.



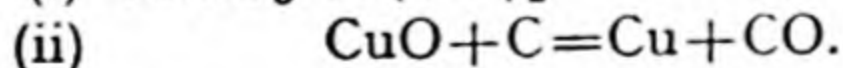
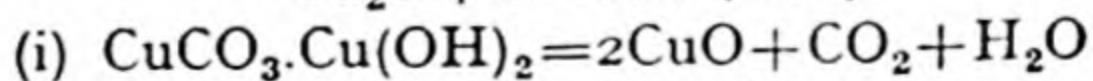
FIG. 63. THE COLOSSUS OF RHODES, FROM AN OLD PRINT

The principal ores of copper are *chalcopyrite*, or *copper pyrites*, CuFeS_2 ; *malachite*, $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$; *azurite*, $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$; *cuprite*, or *ruby ore*, Cu_2O ; *copper glance*, Cu_2S ; and *atacamite*, $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$. The chief countries in which copper is produced are the United States, South America, Japan, Spain, and Germany.

Extraction. The extraction of the metal from its oxide and carbonate ores is a simple matter. They are mixed with a flux (to form a slag with earthy impurities) and heated with powdered anthracite or coke in a reverberatory furnace:



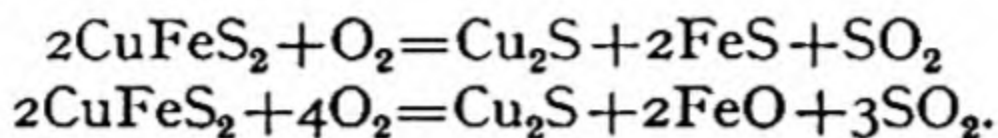
or



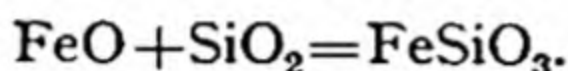
Sulphide ores, which are by far the more important, present great technical difficulties, and the processes employed are so varied as

almost to be peculiar to each individual works. In broad outline, a representative method is as follows.

The crude ore is ground, and concentrated by oil-flotation (p. 353). The concentrated ore is then roasted in a current of air, which removes arsenic as the volatile oxide, As_2O_3 , and much of the sulphur as sulphur dioxide: *

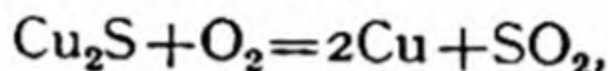


The roasted ore, which may be regarded as a mixture of cuprous and ferrous sulphides with ferrous oxide, is smelted with sand or other siliceous material in a reverberatory furnace, when the ferrous oxide is converted into a fusible slag of ferrous silicate:

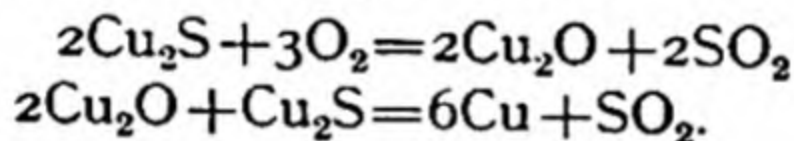


The slag is less dense than, and immiscible with, the mixture of fused sulphides, and the latter is tapped off as *coarse metal* or *copper matte*. Repetition of the process of roasting and fusing with siliceous material yields *fine metal*, which contains about 75 per cent of copper and consists chiefly of cuprous sulphide.

The fine metal is next fused in a Bessemer converter lined with magnesite (MgCO_3) and a regulated blast of hot air is blown through it. The net reaction that takes place is:



though possibly intermediate stages occur:



The molten metal is run off into moulds. As it cools, the sulphur dioxide and residual oxygen and nitrogen retained in it escape, forming blow-holes within and blisters without ('blister copper').

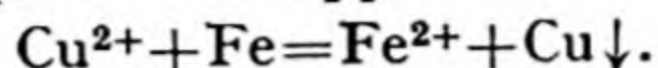
The copper thus obtained still contains 2-4 per cent of impurities, chiefly iron and sulphur with smaller quantities of arsenic, antimony, bismuth, lead, zinc, silver, and gold. It is refined electrolytically, the blister copper being cast into blocks which are made the anodes in an electrolytic bath of copper sulphate solution acidified with sulphuric acid. The cathodes are thin sheets of pure copper. On passing the current, copper is dissolved from the anodes and deposited on the cathodes, while the impurities either pass into solution (Fe, As, Sb, Bi, Zn) or are deposited round the anode (Pb,† Ag, Au) as a slime—the 'anode slime'—which may be

* This may be delivered to a sulphuric acid plant.

† This presumably dissolves at first, but is precipitated as lead sulphate.

rich enough in the precious metals to make their recovery from it profitable.

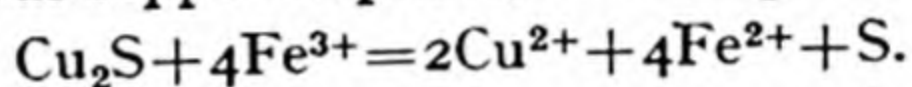
Wet Processes. (i) In the Rio Tinto district of Spain, copper pyrites is crushed and exposed to the air for some months in the presence of water; if the rainfall is insufficient, water is sprayed over the heaps from hose-pipes. The sulphides gradually oxidize to sulphates, which are dissolved out, and the solution is treated with scrap iron, to precipitate the copper:



The copper powder is made into blocks by fusion and solidification, and is then refined electrolytically.

(ii) Low grade malachite ores are often crushed and leached out with ammonium carbonate solution. This dissolves the copper of the ore as cupric ammonium carbonate, and when the solution is boiled a precipitate of cupric oxide and basic cupric carbonate is formed. Copper is obtained from the precipitate by smelting with carbon.

(iii) Low grade sulphide ores are crushed and extracted with a solution of ferric sulphate acidified with sulphuric acid; the copper goes into solution as copper sulphate, and is separated by electrolysis:



Uses of Copper. Copper is mainly used as an electrical conductor. For this purpose it must be extremely pure, since its conductivity is greatly reduced by the presence of impurity, even in traces. Copper is also used for making steam-pipes (since it is unattacked by steam), for sheathing ships, for electroplating and electrotyping, and in the manufacture of alloys. *Brass* is an alloy of copper and zinc containing 18–35 per cent of zinc. *Bronze* contains copper (about 80 per cent) and tin (5–20 per cent), sometimes with the addition of zinc and a little lead. It is used for coinage. *Nickel silver* has the approximate composition Cu 60, Zn 20, Ni 20 per cent. *Monel metal* (p. 602) contains about 32 per cent of copper and 65 per cent of nickel. *British silver coinage* was an alloy of copper, silver, nickel, and zinc. Many copper compounds, such as copper sulphate (q.v.), have important industrial, agricultural, or technical applications. The annual production of copper is about 1,500,000 tons, of which more than 1,000,000 tons are used for electrical purposes.

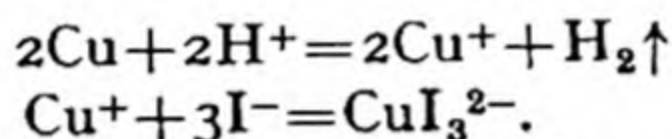
Properties. Copper is a rosy-pink metal, very malleable and ductile and an excellent conductor of heat and electricity. It melts at $1,083^\circ$, boils at $2,300^\circ$, and has a specific gravity of 8.95.

Copper compounds are poisonous, and may cause serious illness ending in death, though in small quantities (as in preserved vegetables with copper chlorophyll) they may be habitually consumed with no apparent ill effects.

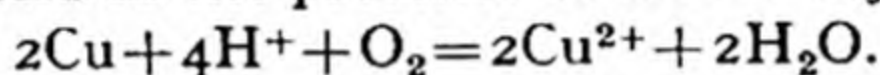
Copper is stable in dry air at ordinary temperatures, though a bright copper surface quickly tarnishes owing to the formation of a thin film of oxide or sulphide. In moist air, copper objects slowly become covered with a green coating,* or patina, consisting of a basic sulphate, $\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2$, less frequently a basic carbonate, $\text{CuCO}_3 \cdot 3\text{Cu}(\text{OH})_2$, or — in maritime regions — a basic chloride (atacamite), $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$.

When heated in air or oxygen, copper becomes coated with a black layer of cupric oxide, under which is a pink layer of cuprous oxide. Prolonged heating converts the whole into cupric oxide—though this, at high temperatures, decomposes into cuprous oxide and oxygen.

Copper is unattacked by pure water, and does not decompose steam below a white heat. As its position in the electrochemical series (p. 244) would indicate, it does not normally dissolve in acids with liberation of hydrogen. It will, however, do so with hydriodic acid, owing to the great readiness with which it forms the complex ion CuI_3^{2-} :



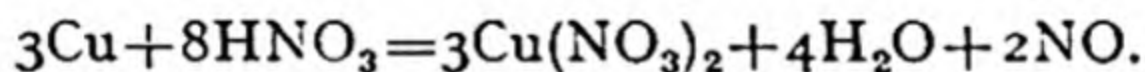
Copper will also slowly dissolve in dilute hydrochloric acid and dilute sulphuric acid in the presence of air or oxygen:



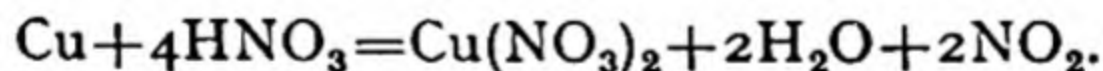
Under similar conditions, even weak organic acids will dissolve it.

Oxidizing acids readily attack copper. Hot concentrated sulphuric acid converts it into a black mixture of cupric sulphate, cupric sulphide, and cuprous sulphide, with evolution of sulphur dioxide; the reaction is complex and cannot be represented by a single equation.

Dilute nitric acid dissolves copper, mainly according to the equation:



Concentrated nitric acid is reduced less far, namely to nitrogen dioxide:



Both of the last two equations are to be considered as mere approximations.

Copper is not attacked by alkalis, though it will dissolve in ammonia solution in the presence of air.

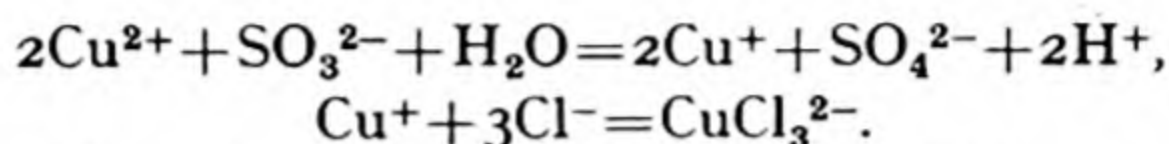
Copper forms two series of compounds: the *cuprous*, in which it is univalent, and the *cupric*, in which it is bivalent. The cuprous

* Sometimes, though incorrectly, called *verdigris*, a name which is properly applied to basic cupric acetate (q.v.).

ion, Cu^+ , is colourless and unstable in aqueous solution; the (hydrated) cupric ion, Cu^{2+} , is blue and stable.

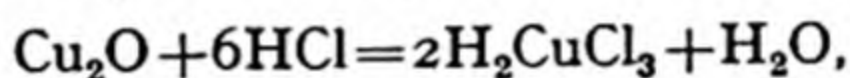
CUPROUS COMPOUNDS

Cuprous oxide, Cu_2O , is prepared in the following way. A solution of cupric sulphate is added slowly to a hot solution containing sodium sulphite and sodium chloride, when a colourless solution results, containing cuprous chloride dissolved as the chlorocuprous anion:

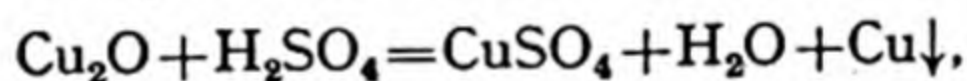


On mixing with a hot solution of borax (which acts as a dilute solution of sodium hydroxide) the anion is decomposed and a crystalline precipitate of cuprous oxide is obtained.

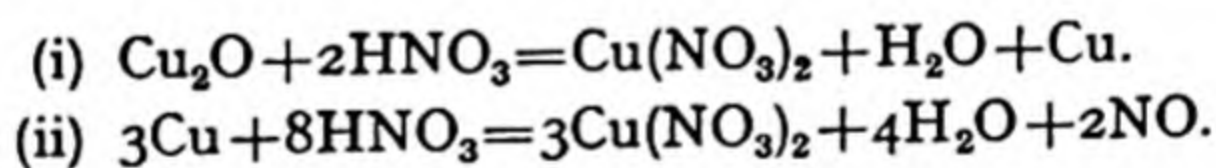
Cuprous oxide is a red powder (M.P. $1,235^\circ$) insoluble in water, but soluble in acids to give cuprous compounds, if these are stable, or a mixture of the cupric salts with copper (the latter may itself react with the acid). Thus it dissolves in concentrated hydrochloric acid to form chlorocuprous acid:



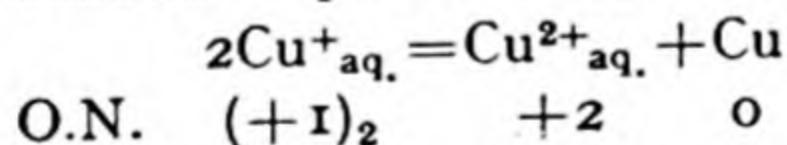
reacts with dilute sulphuric acid to give cupric sulphate and copper:



and dissolves in dilute nitric acid with evolution of oxides of nitrogen:



These latter reactions depend on the change

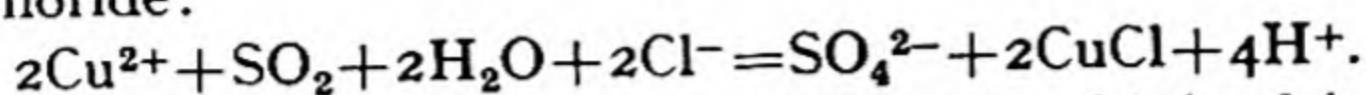


which is a simple example of *disproportionation*, that is a spontaneous change in which an ion or molecule yields products of higher and lower oxidation numbers than itself. The uncatalysed decomposition of potassium chlorate and its action with sulphuric acid (p. 307) are other instances of this process.

When heated moderately in air or oxygen, it is oxidized to cupric oxide, CuO ; above $1,000^\circ$, however, the cupric oxide decomposes again into cuprous oxide and oxygen. Cuprous oxide is used in electrical rectifiers, e.g. battery chargers, and in making red glass.

Cuprous chloride, CuCl , is formed when copper is heated in hydrogen chloride (or in chlorine if the temperature is sufficiently

high). It is preferably prepared by passing a stream of sulphur dioxide through a solution of cupric sulphate with its equivalent of sodium chloride:

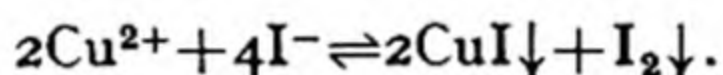


The precipitate of cuprous chloride directly obtained is washed with *ice-cold* water, and then with alcohol and ether to dry it.

Cuprous chloride, so prepared, is a colourless crystalline solid (M.P. 422°), stable in dry air but quickly turning green in moist air owing to oxidation to basic cupric chloride, $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$. Warm water hydrolyses it to cuprous oxide and hydrochloric acid, and boiling water converts it into cupric chloride and copper. It dissolves readily in aqueous ammonia, to give a solution (*ammoniacal cuprous chloride*) which is colourless in complete absence of oxygen, but which is usually dark blue owing to oxidation; it contains the complex ion $[\text{Cu} \cdot 2\text{NH}_3]^+$ and absorbs carbon monoxide, forming a carbonyl compound said to have the composition $\text{CuCl} \cdot \text{CO} \cdot \text{H}_2\text{O}$. It also gives a brown precipitate of *cuprous acetylide*, Cu_2C_2 , with acetylene.

Vapour density determinations show that the vapour of cuprous chloride consists of the double molecules Cu_2Cl_2 .

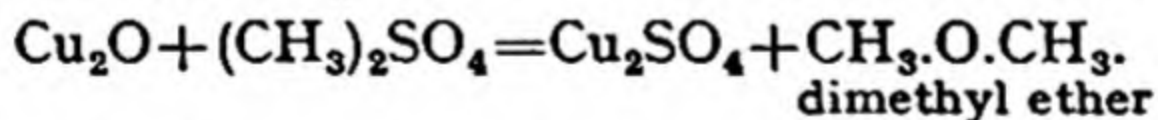
Cuprous iodide, CuI , is a colourless solid precipitated when potassium iodide solution is added to a solution of a cupric salt:



The precipitate is coloured by the iodine liberated at the same time.

This reaction is used in the volumetric estimation of copper, the iodine being titrated with standard sodium thiosulphate. As the reaction is reversible it is essential to use a large excess of potassium iodide in applying this quantitative method.

Cuprous sulphate, Cu_2SO_4 , is a white powder prepared by heating methyl sulphate with cuprous oxide in the absence of air:



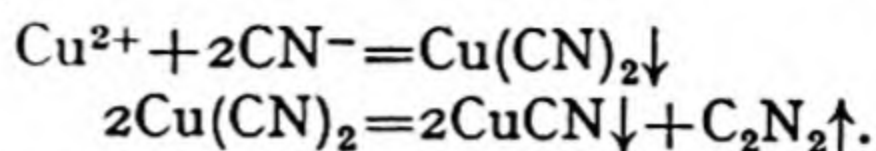
It is immediately decomposed by water into cupric sulphate and copper.

Cuprous nitrate, CuNO_3 , has not been isolated, but is known in the form of complex organic compounds, e.g. with acetonitrile, $\text{CH}_3 \cdot \text{CN}$.

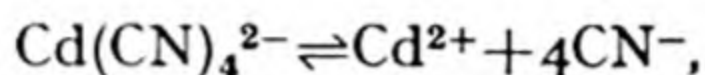
Cuprous sulphide, Cu_2S , occurs naturally as copper glance, and can be synthesized by heating copper and sulphur together in the proportions demanded by the formula.

Cuprous cyanide, CuCN , is formed when potassium cyanide solution is added to a solution of a cupric salt, the original yellow

precipitate of cupric cyanide rapidly decomposing into cyanogen and cuprous cyanide:



It is a white solid, soluble in excess of potassium cyanide solution to give the complex ion $\text{Cu}(\text{CN})_4^{3-}$ of *potassium cuprocyanide*. A solution of this compound contains so few cuprous ions that it gives no precipitate with hydrogen sulphide. The similar complex ion $\text{Cd}(\text{CN})_4^{2-}$ formed by cadmium, on the other hand, is partially dissociated:



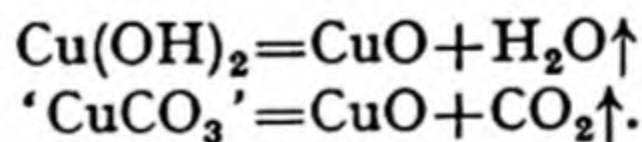
and yields a sufficiently high concentration of cadmium ions for the solubility product of cadmium sulphide to be exceeded on passage of hydrogen sulphide. This difference of behaviour is used in qualitative analysis to separate cadmium from copper.

It will have been noticed that the only soluble cuprous compounds are those in which the simple ion Cu^+ is combined in a complex ion, e.g. CuCl_2^{2-} , $(\text{Cu} \cdot 2\text{NH}_3)^+$, $\text{Cu}(\text{CN})_4^{3-}$, sufficiently stable to resist disproportionation.

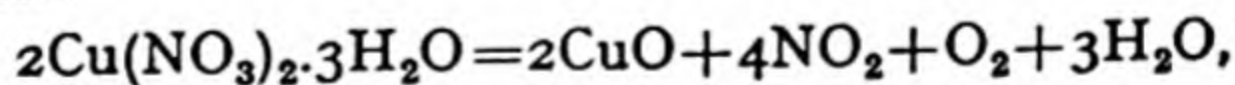
CUPRIC COMPOUNDS

The cupric ion, Cu^{2+} in aqueous solution, is probably more correctly written $[\text{Cu} \cdot 4\text{H}_2\text{O}]^{2+}$.

Cupric oxide, CuO , can be made by heating copper in air or oxygen, but unless the copper is finely divided complete oxidation is a very slow process. It is therefore better to prepare the oxide by heating the hydroxide, 'carbonate' (p. 319), or nitrate:



The decomposition of the nitrate, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, is complex; the equation:

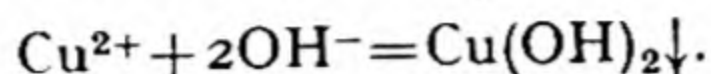


is inaccurate, since nitric acid is one of the products.

Cupric oxide is a black hygroscopic solid used in organic analysis (e.g. combustions) as an oxidizing agent. It is readily reduced to metal by heating with carbon, or in hydrogen. If heated alone to a high temperature ($1,000^\circ$) it decomposes into cuprous oxide and oxygen.

It is a basic oxide, dissolving in dilute acids to form the corresponding cupric salts.

Cupric hydroxide, $\text{Cu}(\text{OH})_2$, is obtained as a Cambridge-blue gelatinous precipitate when a solution of sodium hydroxide is added to a solution containing cupric ions:



(If the cupric salt used is the sulphate, the precipitate of the hydroxide carries some of the sulphate with it.)

The pale blue hydroxide turns black when boiled with water, owing to partial dehydration into $3\text{CuO} \cdot \text{Cu}(\text{OH})_2$. This loses its last molecule of water only at a red heat.

When ammonia solution is added to cupric hydroxide, the latter dissolves, forming a deep blue liquid (SCHWEITZER'S solution) containing the *tetrammino-cupric* ion $[\text{Cu} \cdot 4\text{NH}_3]^{2+}$. Schweitzer's solution has the power of dissolving cellulose,* which is re-precipitated if the solution is acidified. By squirting the solution in fine jets into dilute acid, the cellulose is formed in silky threads, which can be spun and woven into 'cuprammonium rayon'—one variety of artificial silk.

Cupric carbonate is unknown as the pure normal salt. When sodium carbonate solution is added to a solution of a cupric salt, a pale bluish-green precipitate ('verditer') is obtained, but this is a basic carbonate and sometimes contains sodium carbonate as well. *Azurite* and *malachite* are natural basic carbonates.

Cupric chloride, CuCl_2 , can be prepared as an anhydrous deliquescent brown solid by *gently* heating copper in an ample supply of chlorine; strong heat must be avoided, for the cupric salt decomposes into cuprous chloride and chlorine at a moderately high temperature.

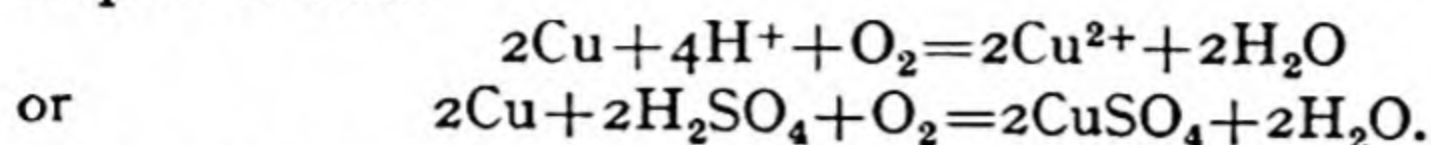
Solutions of cupric chloride, prepared by dissolving the oxide or basic carbonate in hydrochloric acid, deposit crystals of the *dihydrate*, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, on evaporation. This may be dehydrated by heating in a current of hydrogen chloride.

A concentrated solution of cupric chloride is yellow, but on dilution the colour changes to yellowish-green, green, and finally blue. Addition of concentrated hydrochloric acid to the blue solution reverses these colour changes, which are attributed to changes in the relative proportions of cupric ions (blue), undissociated molecules of cupric chloride (yellow), and complex ions CuCl_4^{2-} (yellow).

Cupric sulphate, CuSO_4 . Cupric sulphate is manufactured by

* It must be made by dissolving *washed* cupric hydroxide in ammonia solution. The solution made by adding ammonia solution to copper sulphate solution in sufficient excess to re-dissolve the cupric hydroxide first precipitated is *not* able to dissolve cellulose.

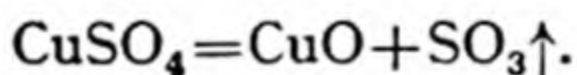
blowing air through a hot mixture of scrap copper and dilute sulphuric acid:



The solution is filtered from impurities and concentrated; on cooling, crystals of cupric sulphate *pentahydrate*, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, separate out. These are known as 'blue-stone,' 'blue vitriol,' or simply as copper sulphate crystals.

Copper sulphate is also manufactured by the regulated roasting of copper pyrites, CuFeS_2 , in a current of air; the copper is largely converted into copper sulphate, while the iron is oxidized to ferric oxide. The roasted mass is then extracted with water and the solution of copper sulphate concentrated.

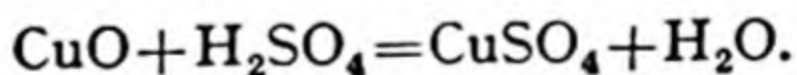
When gently heated (110°), the pentahydrate loses four molecules of water of crystallization, and the nearly colourless *monohydrate*, $\text{CuSO}_4 \cdot \text{H}_2\text{O}$, is formed. On further heating (290° – 300°), the last molecule of water may be driven off, leaving a whitish residue of the anhydrous salt. Anhydrous copper sulphate readily re-combines with water, to form the blue pentahydrate, and this change is used as a test for water, e.g. in alcohol. On strong heating (700°), the anhydrous salt is itself split up into copper oxide and sulphur trioxide:



Copper compounds are good fungicides, and are used in spraying potatoes and vines. The spraying mixtures usually consist of copper sulphate solution mixed with lime ('Bordeaux mixture') or washing-soda. A handful of copper sulphate crystals dissolved in two gallons of water makes a useful liquid with which to spray a lawn to remove worms; it should be applied when the ground is thoroughly moist, and after about twenty minutes the worms may be swept up.

Copper sulphate is also used in electroplating, in calico-printing, in making various dyes, and in the preservation of wood from rot.

In the laboratory, copper sulphate is conveniently prepared by dissolving cupric oxide in dilute sulphuric acid:



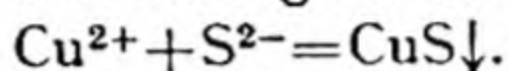
The chief impurity in the commercial product is ferrous sulphate. This may be removed by boiling the solution with a little nitric acid to convert the ferrous sulphate into ferric sulphate, and crystallizing. The ferric sulphate is much more soluble than the copper sulphate and is left in the mother-liquor.

Addition of excess of ammonia solution to a solution of copper sulphate yields a dark blue solution from which alcohol precipitates

purple crystals of *tetrammino-cupric sulphate monohydrate* ('cuprammonium sulphate'), $[\text{Cu} \cdot 4\text{NH}_3]\text{SO}_4 \cdot \text{H}_2\text{O}$. This should not be confused with the double salt *copper ammonium sulphate*, $(\text{NH}_4)_2\text{SO}_4 \cdot \text{CuSO}_4 \cdot 6\text{H}_2\text{O}$, which is a pale blue crystalline solid isomorphous with ferrous ammonium sulphate (p. 592); it can be made by crystallizing a solution containing equivalent weights of ammonium sulphate and copper sulphate.

Cupric nitrate, $\text{Cu}(\text{NO}_3)_2$, is obtained in blue deliquescent crystals of the *trihydrate*, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, when its aqueous solution—prepared in any of the usual ways—is evaporated. It is a powerful oxidizing agent, and a mixture of it with tin foil may inflame.

Cupric sulphide, CuS , is precipitated as a black solid when hydrogen sulphide is passed through a solution of a cupric salt:



On exposure to moist air it is slowly converted into copper sulphate (or basic sulphate). When strongly heated, it decomposes into cuprous sulphide and sulphur.

Cupric acetate. A basic cupric acetate, $(\text{CH}_3\text{COO})_2\text{Cu} \cdot \text{Cu}(\text{OH})_2$, is the important green pigment *verdigris*.

Tests for Copper.

1. Flame: bluish-green.
2. Borax bead: pale blue (oxidizing flame), or red (reducing flame).
3. Charcoal block: red spangles of metallic copper.
4. Solutions of *cupric* salts are generally blue or green, and give with:
 - (a) hydrogen sulphide: black precipitate of cupric sulphide;
 - (b) sodium hydroxide: pale blue precipitate of cupric hydroxide;
 - (c) ammonia solution: pale blue precipitate of cupric hydroxide, soluble in excess to a deep blue solution containing the tetrammino-cupric ion, $[\text{Cu} \cdot 4\text{NH}_3]^{2+}$.
 - (d) potassium ferrocyanide: brown precipitate of *cupric ferrocyanide*, $\text{Cu}_2\text{Fe}(\text{CN})_6$, insoluble in dilute acids but soluble in ammonia to give a blue solution.

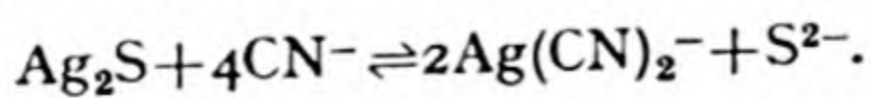
SILVER, Ag

Atomic number: 47. *Atomic weight:* 107.880. *Specific gravity:* 10.5.
Melting-point: 960°. *Boiling-point:* 1,950°.

History. Since silver occurs native, and is also easily extracted from its ores, it has been known from very ancient times. During the Old Empire (3000–2500 B.C.) silver was scarce and costly in Egypt, where it was known as 'white gold' and whither it seems to have been imported from Asia. Later on, however, it was produced in greater abundance, and its relative value to gold sank to about 1 to 10 or 1 to 13; in the time of SOLOMON it was held in little account. The silver mines at Laurium, near Athens, were worked as early as the sixth century B.C., and in 484 B.C. they yielded about 84,000 ounces troy to the Athenian treasury. On the advice of THEMISTOCLES, the money was used to build a fleet, and was thus very timely; for when, four years later, the Persians attacked Greece, they were heavily defeated in the naval action at Salamis. The process of cupellation (p. 323) is mentioned by PLINY (first century A.D.), and the 'parting' of gold and silver by means of nitric acid is described by Arabian chemists of the thirteenth century. Among the alchemists, silver was considered to be under the special influence of the moon, and was thus often called *Luna* and given the symbol of the lunar crescent, \mathcal{D} . A relic of this doctrine is to be found in the pharmacists' name for silver nitrate—*lunar caustic*.

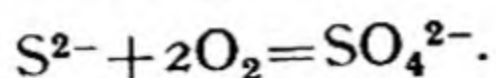
Occurrence. The principal forms in which silver is found are native silver (Peru, Idaho, etc.), *argentite* or *silver glance*, Ag_2S ; *red silver ore*, *pyrargyrite*, or *ruby-silver*, $3\text{Ag}_2\text{S} \cdot \text{Sb}_2\text{S}_3$; *horn-silver* or *chlorargyrite*, AgCl ; and *stephanite*, Ag_5SbS_4 . Large quantities of silver are also extracted from galena (p. 418), which is always argentiferous and occasionally contains a comparatively high percentage of silver. The principal silver-producing countries are (in order of output): Mexico, United States, Canada (especially the Cobalt district of Ontario), and Peru. The annual production has risen from about 1,500,000 ounces in A.D. 1500 to over 200,000,000 ounces at the present time.

Extraction. For the extraction of silver from its sulphide ore, the ore is finely crushed and then steeped in sodium cyanide solution for some time, a current of air being blown through the liquid. The silver sulphide dissolves as sodium argentocyanide:

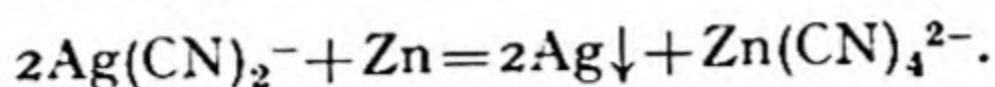


This reaction is reversible, and the purpose of the current of air is to

prevent the right-to-left change by removal of the sulphide ions as sulphate and thiosulphate ions:



From the sodium argentocyanide solution, the silver is precipitated by addition of aluminium or zinc:



Desilverization of Lead. When lead is extracted from argentiferous galena, the silver in the ore remains in the lead. The mixture is concentrated by melting it and allowing it to cool, when the first crystals to separate are of pure lead. These are removed, and the process (PATTINSON'S process) is repeated until the remaining alloy contains about 1 per cent of silver. In PARKES'S process, a little zinc is added to the molten argentiferous lead, upon which it melts, and with which it is nearly immiscible. Silver is much more soluble

in zinc than in lead, the distribution ratio $\frac{C_{\text{Zn}}}{C_{\text{Pb}}}$ being about 300 at

800°; hence a rich silver-zinc alloy is formed. This rises to the surface as solid crystals, which are removed with a perforated ladle. More zinc is then added, and the operation repeated until the lead contains no more than 0.0005 per cent of its weight of silver. The silver-zinc alloy (which carries some lead with it) is distilled, when the zinc volatilizes, and a residue of silver, alloyed with lead, remains in the retort.

The silver-lead alloys obtained by the Pattinson and Parkes processes are freed from lead by *cupellation*. A shallow bowl or tray, made of marl, bone-ash, cement, or some similar material, and known as a *cupel*, is filled with the alloy and heated in a current of air. The alloy melts, and the lead it contains is oxidized to litharge (PbO) (hence this name for lead oxide, from the Greek *lithargyros*, silver stone). Some of the litharge is absorbed by the cupel, but most is blown over the edge. After a time, the layer of litharge on the surface of the molten silver is so thin that iridescent colours appear, and shortly afterwards the bright silver 'flashes' in undimmed radiance.

Cupellation is also employed to refine the crude silver obtained in the cyanide process. Alternatively silver may be refined by electrolysis, using as the electrolyte a solution of silver nitrate acidified with nitric acid. The impure silver is made the anode, and a sheet of pure silver forms the cathode. Upon electrolysis, silver is transferred from the anode to the cathode, while impurities either go into solution (e.g. copper) or are precipitated round the anode (e.g. gold).

Electroplating. Silver deposited electrolytically from silver nitrate solution does not form an adherent coating upon the cathode. In electroplating, therefore, where it is essential that the silver layer should be firmly coherent and adherent, the electrolyte employed is a solution of potassium argentocyanide. The article to be plated is made the cathode, the anode being a block of pure silver.

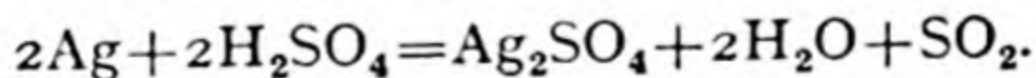
Copper articles can be electroplated directly. Iron articles must first be coated with copper, since iron is so high in the electrochemical series (p. 244) that it precipitates silver even from a solution of potassium argentocyanide.

Properties. Silver is a pure white metal, which melts at 960° and boils at $1,950^{\circ}$ to give a blue vapour. It is comparatively soft, so that for making coins, jewellery, table silver, and the like, it is alloyed with copper or nickel to render it harder.

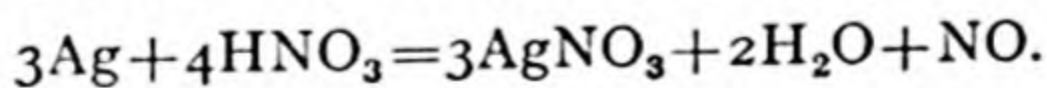
Silver is malleable and ductile, and conducts heat and electricity better than any other metal. It is stable in pure air, but town air, which always contains traces of hydrogen sulphide, slowly tarnishes its lustre with a film of black silver sulphide, Ag_2S . The same blackening occurs when a silver spoon is placed in an egg—especially an egg of some age—since eggs contain sulphur compounds (proteins). The tarnishing may be prevented, without loss of beauty, by plating the silver with a thin coating of rhodium; this is perfectly resistant even to hydrogen sulphide, and has the exact appearance of highly polished silver. The so-called 'oxidized silver' is silver deliberately coated with silver sulphide by dipping it into a solution of ammonium sulphide.

Silver does not apparently combine with oxygen on heating, but molten silver at its melting-point has the remarkable property of absorbing over twenty times its own volume of the gas; this is expelled energetically as the silver solidifies, causing the phenomenon known as 'spitting.' Possibly some at least of the absorbed oxygen combines with silver to form silver oxide, and this decomposes sharply when solidification occurs.

Like copper, below which it comes in the electrochemical series, silver will not dissolve in dilute hydrochloric or dilute sulphuric acid. Hot concentrated sulphuric acid converts it into silver sulphate, with evolution of sulphur dioxide:



It dissolves in nitric acid, nitric oxide being given off:



Unlike gold, it does not dissolve in aqua regia (HNO_3 , 1; HCl , 3), which converts it into the insoluble silver chloride, AgCl . Alkalis have no action upon it.

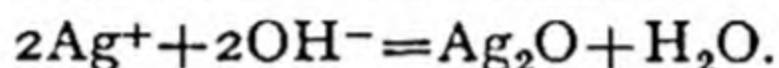
Silver may be obtained in the *colloidal state* (p. 262), and as a thin film on glass—a *silver mirror*. To silver a glass flask, the flask is filled with ammoniacal silver nitrate (see below) and a little glucose is added. Upon warming, reduction takes place and the mirror is formed.

COMPOUNDS OF SILVER

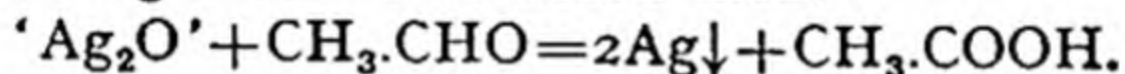
Silver forms two series of compounds, the *argentous* and the *argentic*, in which it is univalent and bivalent respectively. The former are by far the more important, few argentic compounds having yet been prepared. *Argentic fluoride*, AgF_2 , is a brown solid made by the action of fluorine upon silver at ordinary temperatures.

The unipositive silver ion, Ag^+ , is colourless.

Silver oxide, Ag_2O , is thrown down as a brownish-black precipitate when an alkali-metal hydroxide or ammonia solution (in limited amount) is added to silver nitrate solution:



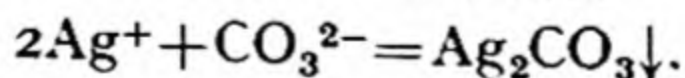
The oxide is insoluble in excess of caustic alkali, but dissolves readily in excess of ammonia solution, forming the complex ion $\text{Ag}(\text{NH}_3)_2^+$. The solution made by adding ammonia to silver nitrate solution until the precipitated oxide has just re-dissolved is known as *ammoniacal silver nitrate* (or *ammoniacal silver oxide*) and is used in organic chemistry as a test for reducing agents, which reduce it to metallic silver. Thus, with acetaldehyde, it gives a silver mirror, the acetaldehyde being oxidized to acetic acid:



Ammoniacal silver nitrate should not be left exposed to the air, since on oxidation it slowly deposits an explosive black solid, possibly silver nitride, Ag_3N .

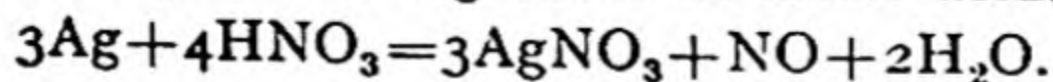
Silver oxide readily decomposes into its elements when gently heated. When moist, it often behaves as though it were *silver hydroxide*, but this compound has no individual existence.

Silver carbonate, Ag_2CO_3 , is formed as a pale yellow precipitate when sodium or potassium carbonate is added to silver nitrate solution; or, in crystalline condition, by passing a stream of carbon dioxide through ammoniacal silver nitrate:



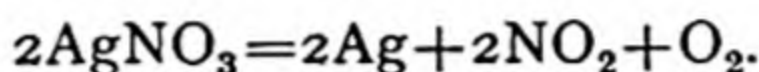
On heating it decomposes into silver oxide and carbon dioxide, or, at a higher temperature, into silver, oxygen, and carbon dioxide.

Silver nitrate, AgNO_3 , is a colourless crystalline anhydrous solid (M.P. 218°) made by dissolving silver in nitric acid.

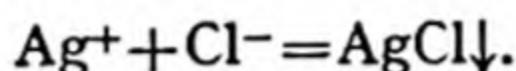


It readily oxidizes organic matter, by which it is itself reduced to metallic silver. Upon this property depends its use, in solution, as marking-ink; silver is deposited in the textile fibres and cannot be removed by washing. The caution not to heat freshly marked articles is necessary to prevent excessive oxidation of the fabric, which might thus be ruined. The black stains left on the fingers by silver nitrate solution also consist of silver formed in a similar way.

Upon heating, silver nitrate decomposes into silver, oxygen, and nitrogen dioxide:



Silver nitrate is widely used as a volumetric reagent, in the estimation of chlorine ions:



The equivalent of the salt is $(108 + 14 + 48)$, i.e. 170, so that 1 litre of the decinormal solution contains 17.0 gm. AgNO_3 and is equivalent to 3.55 gm. of chlorine ion. Potassium chromate may be used as indicator, if the solutions are neutral. The solubility product of silver chromate, $[\text{Ag}^+]^2[\text{CrO}_4^{2-}]$, is 2.0×10^{-12} , and that of silver chloride 1.0×10^{-10} . Hence if potassium chromate is added until $[\text{CrO}_4^{2-}]$ is 0.01, then silver chromate will be precipitated when

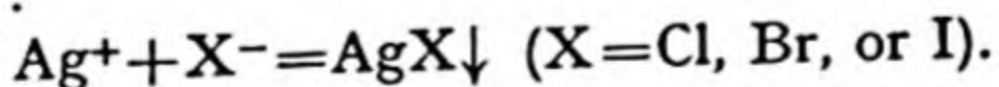
$$[\text{Ag}^+]^2 = (2.0 \times 10^{-12}) \times 10^2;$$

that is, when

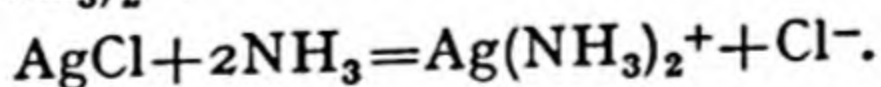
$$[\text{Ag}] = 1.4 \times 10^{-5}.$$

But at the equivalence point for the titration, $[\text{Ag}^+] = [\text{Cl}^-] = 10^{-5}$. It follows that, provided the amount of indicator is properly adjusted, a precipitate of silver chromate will only be permanent at and beyond the end-point. Adsorption indicators (p. 266) are now preferred.

Silver chloride, AgCl , can be prepared from its elements, since silver readily combines with chlorine. It is, however, usually obtained by mixing silver nitrate solution with a solution of a soluble chloride, when it is precipitated in the form of white curds. The *bromide* (pale yellow) and *iodide* (yellow) may be prepared in a similar manner:



Silver chloride dissolves easily in aqueous ammonia, forming the complex ion $\text{Ag}(\text{NH}_3)_2^+$:

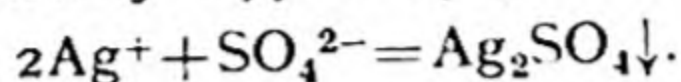


The bromide dissolves less easily, while the iodide is almost insoluble. Silver chloride will also dissolve in potassium cyanide solution. With gaseous ammonia it yields additive products, $x\text{AgCl} \cdot y\text{NH}_3$.

Silver halides darken on exposure to light (see below).

Silver may be recovered from silver chloride 'residues' by boiling with potassium hydroxide solution and glucose. Silver oxide is first formed, and this is reduced to silver by the glucose.

Silver sulphate, Ag_2SO_4 , is a colourless, crystalline solid obtained by the addition of a soluble sulphate to a solution of silver nitrate. The solutions must not be too dilute, since silver sulphate is slightly soluble in water (solubility 0.77 at 17°):



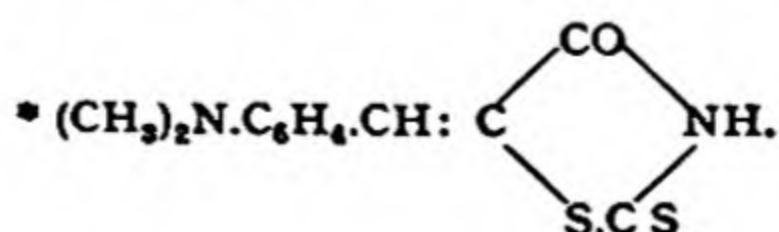
Tests for Silver.

Silver salts in solution give with

- (a) dilute hydrochloric acid: white precipitate of silver chloride, AgCl , insoluble in concentrated nitric acid, soluble in ammonia solution;
- (b) potassium chromate: brick-red precipitate of silver chromate, Ag_2CrO_4 , soluble in dilute nitric acid;
- (c) a dilute acetone solution of p-dimethylaminobenzalrhodamine* (spot test): reddish brown precipitate. This test is exceedingly delicate.

Photography. Many silver salts are reduced to metallic silver by the action of light, and it is upon this fact that photography (Greek 'light-writing') is based. It was known as early as 1565 that silver salts darken on exposure to light, but the first photographs seem to have been obtained in 1802, by THOMAS WEDGWOOD (1771-1805), son of Josiah Wedgwood, the celebrated potter. Wedgwood used silver nitrate as the sensitive salt, but as he could not remove the unaffected parts of the substance the images were not stable in the light. During the next two or three decades, the brothers NIEPCE experimented with a film of silver chloride on paper, and since SIR JOHN HERSCHEL had discovered (1819) that silver chloride can be dissolved in sodium thiosulphate solution, the production of permanent photographs was now possible.

Instead of developing along the lines thus indicated, however, photography next followed a detour in the work of DAGUERRE (1789-1851). Daguerre at first worked in collaboration with J. N. NIEPCE, but after the latter's death in 1839 he continued the experiments alone. As the result of a fortunate accident, Daguerre had observed (a) that a silver plate exposed to the vapour of iodine

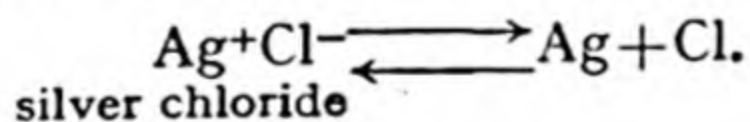


became sensitive to light—owing, of course, to the formation of silver iodide upon its surface—and (b) that an image formed upon such a plate could be developed by exposing it to warm mercury vapour. Fixing was effected by means of sodium thiosulphate ('*hypo*'). The *daguerreotype* process, as it was called, became very popular, and many examples of portraits taken in this way are still to be seen. It should be noted that the daguerreotype image was positive from the start, not negative as with modern plates and films.

Present-day processes have developed from the work of the Englishman FOX TALBOT, who was born at Lacock Abbey, near Chippenham, Wiltshire, in 1800, and died there in 1877. He was a man of great and varied attainments, for he not only made important discoveries in photography but was one of the first to decipher the cuneiform signs of Assyria, wrote a book on English etymologies, and became a member of Parliament.

Fox Talbot's process was to obtain the image on paper coated with silver chloride, develop it with a solution of gallic acid, and fix it with a solution of sodium thiosulphate—in all essentials the method still employed. The image was, however, a negative one, and positives had to be obtained by printing through the paper, so that the results were not very sharp. The use of glass covered with gelatine to replace paper for the negative was suggested in 1848 by NIEPCE DE SAINT-VICTOR (a nephew of J. N. Niepce), and in 1871 R. L. MADDIX used plates coated with an emulsion of silver bromide in gelatine. In 1889 G. EASTMAN produced the first roll-films, in which the sensitive film was supported on celluloid instead of glass, and in 1891 he introduced the daylight-loading film.

Crystals of silver halides—chloride, bromide, and iodide—consist of a lattice of silver ions and halogen ions, and it has recently been shown that the first action of light upon the salt is to cause the transference of an electron from the halogen ion to the silver ion; in other words, a halogen *atom* and a silver *atom* are formed from the ions, and the halide decomposes into metallic silver and halogen:



The action is, however, reversible, and if the halogen is prevented from escaping it recombines with the silver when the light is cut off. On exposing the silver halide to light in the open, some of the halogen escapes, and a permanent deposit of silver is formed. The same effect is produced more quickly if the halide is mixed with a substance that readily combines with free halogen; fortunately, gelatine is a substance of this kind, so that as well as affording a convenient medium for supporting the halide, it actually plays an

essential role in the changes that take place. Silver citrate is an even better 'acceptor' of halogen, and is mixed with the sensitive substance, silver chloride, in printing-out paper.

The film on a photographic plate or 'film' consists of gelatine in which are suspended minute grains of silver bromide and iodide. It is believed that certain points of these grains are particularly sensitive to light, and experiments indicate that the sensitive nuclei

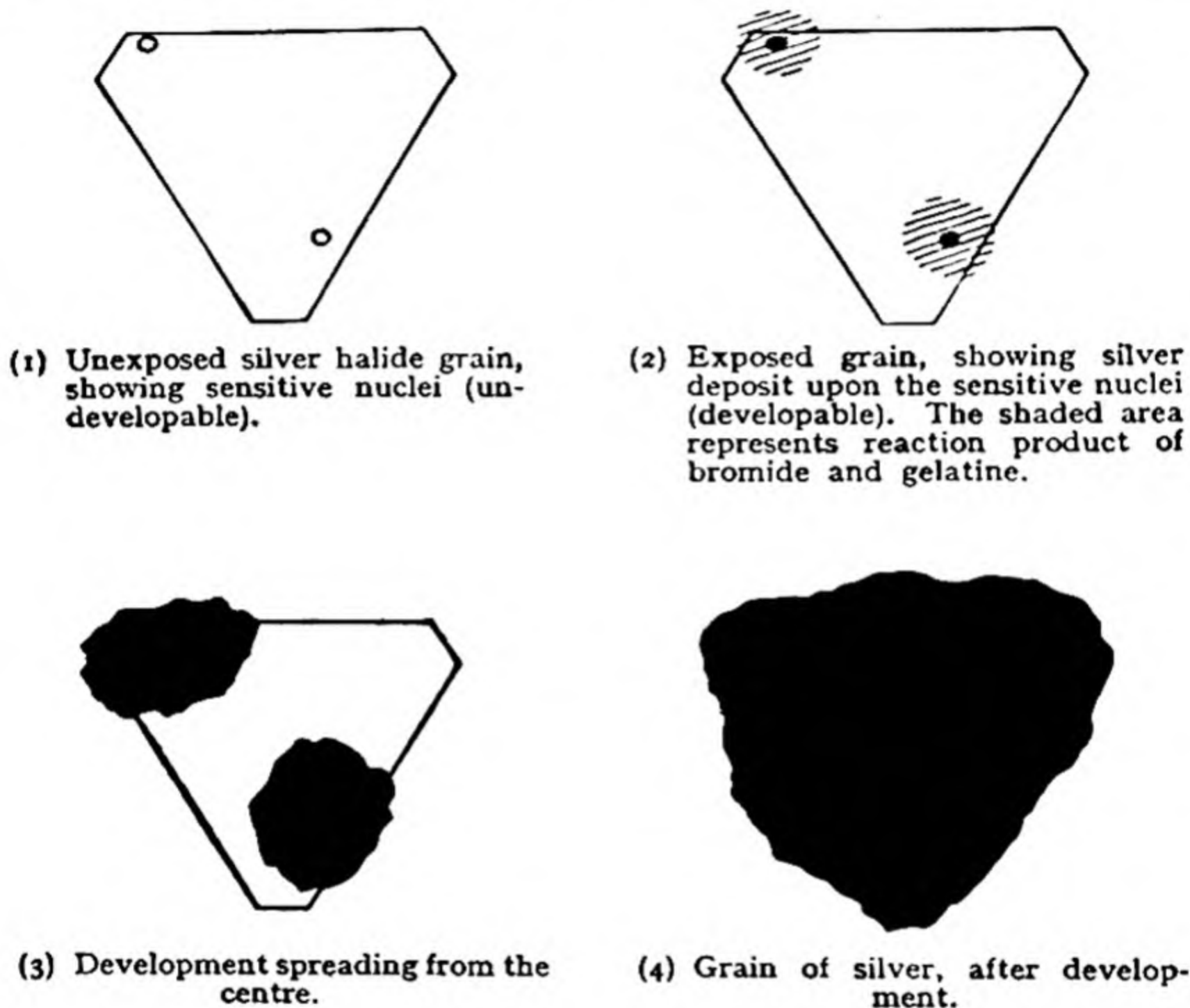


FIG. 64. SUCCESSIVE CHANGES IN SILVER HALIDE PARTICLES

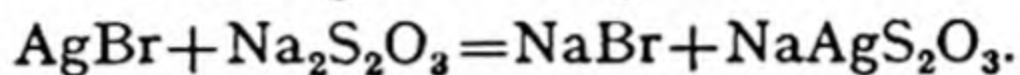
[After Baines]

are composed of substances other than silver halide—perhaps metallic silver, silver oxide, or silver sulphide. On exposure to light, a small quantity of silver bromide in the immediate neighbourhood of the nuclei is reduced to metallic silver, the halogen being taken up by the gelatine. The image so formed is, however, invisible to the naked eye if the exposure is short.

The next stage is development, which consists in immersing the exposed plate in a solution of a suitable reducing agent, such as quinol ('hydroquinone') or pyrogallol in the presence of alkali.

The function of the developer is to continue the reduction of the silver halide, and since this process takes place more rapidly where the initial formation of silver was greater, the image gradually appears but with the light values reversed, i.e. more silver is deposited in those parts of the image where the illumination was great than in those less brightly illuminated. The image is consequently negative.

Development must not be continued too long, or the whole of the silver halide will be reduced to metallic silver and the plate will become uniformly black. It is therefore interrupted when the image has reached the desired depth, and the plate is washed to remove excess of developer which might otherwise stain the gelatine. It is then immersed in the fixing solution, a slightly acid solution of sodium thiosulphate, to dissolve out the unchanged silver halide and so render the image stable to light. The thiosulphate reacts with silver halide according to the equation:



Probably, however, the sodium silver thiosulphate first formed reacts with more sodium thiosulphate to yield such compounds as sodium tri-argento-tetra-thiosulphate, $\text{Na}_5[\text{Ag}_3(\text{S}_2\text{O}_3)_4]$.

Since the blue and violet end of the spectrum is more photochemically active than the red end, an ordinary photographic plate or film does not give an accurate rendering in 'monochrome' of coloured objects. By the addition of certain dyes to the sensitive film, and by the use of coloured light-filters in front of the lens of the camera, this fault can be largely eliminated. Films appropriately sensitive to yellow and green, as well as to blue and violet, are called *orthochromatic*; those sensitive to red in addition are called *panchromatic*.

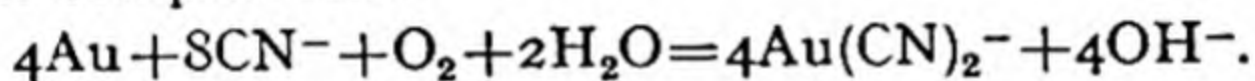
GOLD, Au

Atomic number : 79. Atomic weight : 197.0. Specific Gravity : 19.4.
Melting-point : 1,064°. Boiling-point : 2,200°.

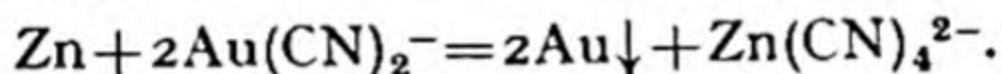
Occurrence and Extraction. Gold, which (like copper and silver) has been known since ancient times, occurs native in masses varying in size from nuggets of over a hundredweight to minute dust-like particles. It is fairly widely distributed, but occurs in workable quantities in only a few countries, of which the chief are South Africa, the United States, Australia, Mexico, and Russia.

Gold is usually found in quartz rocks, or in the alluvial sand formed by the weathering of such rocks. Large particles are extracted by hand, but ore containing small particles is treated by an *amalgamation process*. Mercury is added to the crushed ore and forms an amalgam with the gold. On distillation, the mercury volatilizes and is condensed for further use, while the gold remains.

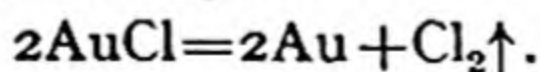
Ore which is too poor to be worked profitably in this way is subjected to the MACARTHUR and FORREST *cyanide process*. This consists in steeping the finely crushed ore in a solution of sodium cyanide in the presence of air, when the gold dissolves as the aurocyanide complex ion:



From the sodium aurocyanide solution the gold is precipitated by the addition of zinc:



Properties and Compounds. Gold is an attractive, bright yellow metal of high density (19.4 gm. per c.c.); it is the most malleable and ductile of all metals, and can be beaten into sheets no thicker than 0.0001 mm. It is highly resistant to chemical action and will dissolve only in those solutions in which it is able to form complex ions. Thus it is unattacked by nitric acid and by hydrochloric acid separately, but dissolves in aqua regia (HNO_3 , 1; HCl , 3) as the chlorauric ion AuCl_4^- . On evaporating the solution, yellow crystals of *chlorauric acid*, $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$, separate out; these on gentle heating (120°) lose water and hydrogen chloride, leaving a residue of *auric chloride*, AuCl_3 . At 175°, auric chloride is converted into *aurous chloride*, AuCl , with evolution of chlorine, and at a higher temperature this in turn decomposes:



In *aurous* compounds gold is univalent; in *auric* compounds it is tervalent. Aurous salts are usually insoluble in water; auric salts

appear to be covalent compounds and are not appreciably ionized in solution.

A *test for gold* in solution is the reddish-violet precipitate formed when the solution is added to a concentrated solution of stannous chloride containing some stannic chloride. This precipitate, known as 'Purple of Cassius,' was discovered by CASSIUS in the seventeenth century and is believed to be a colloidal solution of gold in stannic oxide.

COMPARATIVE EXERCISES

1. Make a comparative table to show the principal resemblances between copper, silver, and gold, and between their chief compounds.

In addition to the points indicated for such a table on p. 310, show any resemblance that exists in the complex ions formed by these three metals.

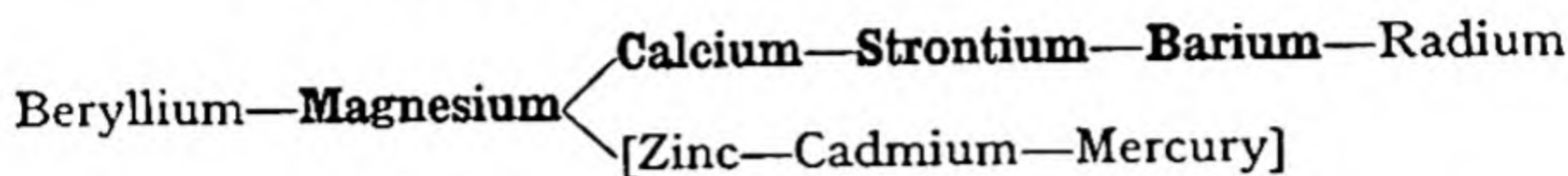
2. Draw up a list of the principal differences between copper, silver, and gold.

3. After reading Chapter XXXI, compare and contrast the properties of copper with those of iron, cobalt, and nickel.

CHAPTER XXIV

GROUP II

MAGNESIUM, CALCIUM, STRONTIUM, BARIUM



Magnesium and the Alkaline-Earth Metals. Calcium, strontium, and barium form (with radium) the 'alkaline-earth' group of metals. The typical element magnesium shows a resemblance both to calcium and to zinc, but is more clearly similar to the former than to the latter.

MAGNESIUM, Mg

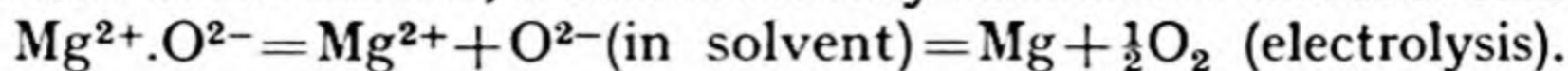
Atomic number: 12. *Atomic weight:* 24.32. *Specific gravity:* 1.74.
Melting-point: 651°. *Boiling-point:* 1,110°.

History. Magnesium sulphate ('Epsom salt') was discovered in the water of a spring at Epsom by NEHEMIAH GREW (1641–1712) in 1695. The composition of *magnesia alba* (a basic magnesium carbonate used in medicine) was elucidated in 1755 by BLACK, and the impure metal was obtained electrolytically by DAVY in 1808. Pure magnesium was first obtained in 1829 by the French physician BRUTUS BUSSY (1794–1882).

Occurrence. Magnesium is too reactive an element to occur in the uncombined state, but its compounds are common and plentiful. Among the chief are *dolomite* (a double carbonate with calcium, $\text{MgCO}_3 \cdot \text{CaCO}_3$), of which the Dolomitic Alps and many other mountain ranges are largely composed; *magnesite*, MgCO_3 ; *carnallite*, $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, and *kainite*, $\text{KCl} \cdot \text{MgSO}_4 \cdot 3\text{H}_2\text{O}$, which occur in the saline deposits at Stassfurt, Germany; *asbestos*, or magnesium calcium silicate, $3\text{MgSiO}_3 \cdot \text{CaSiO}_3$; and *talc*, $3\text{MgSiO}_3 \cdot \text{H}_2\text{SiO}_3$. Magnesium is an essential constituent of chlorophyll, the green colouring-matter of plants.

Extraction. Magnesium is obtained commercially by the electrolysis of magnesium oxide dissolved in a molten mixture of the fluorides of magnesium, barium, and sodium. A diagram of the plant is shown in Fig. 65. The cathodes are of iron and the anodes are of carbon. On electrolysis, molten magnesium forms round the

cathodes and rises to the surface of the molten electrolyte; it is protected from oxidation by a solid crust of the melt. Oxygen is liberated at the anodes, which are slowly oxidized to oxides of carbon:



Another process uses carnallite, $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, as the starting-point. The carnallite is melted and allowed to cool, when potassium

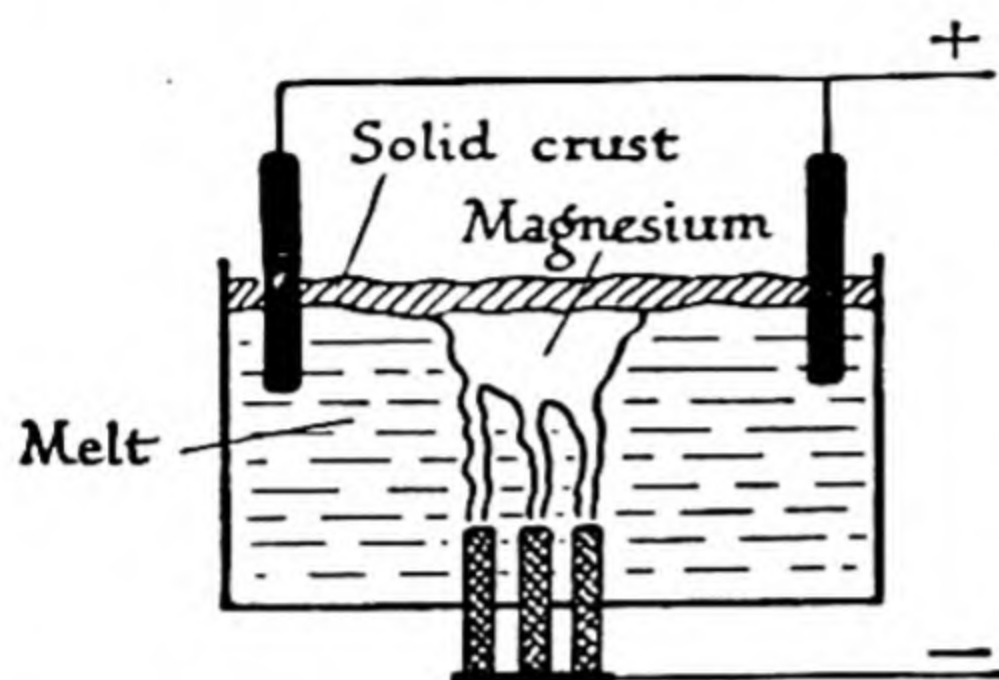


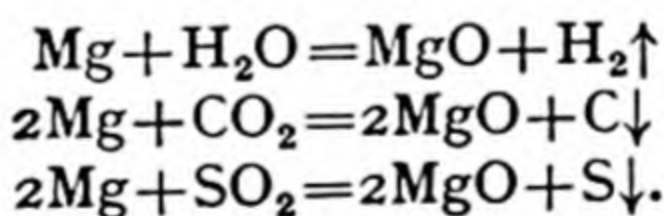
FIG. 65. MANUFACTURE OF MAGNESIUM

chloride crystallizes out first; this is removed and the residual magnesium chloride is dehydrated in a current of hydrogen chloride. The anhydrous chloride is then fused and electrolysed. In America the magnesium chloride is obtained from sea-water.

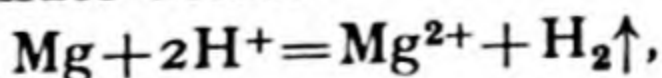
Properties. Magnesium is a white metal of specific gravity 1.74. It melts at 651° and boils at $1,110^\circ$. It is stable in dry air, but

quickly tarnishes in moist air, owing to the formation of the oxide, MgO . When heated in oxygen it burns with an intensely brilliant light, again forming the oxide. If magnesium is burned in the air, the light emitted is less bright—though still dazzling—and the product is a mixture of magnesium oxide, MgO , with a little *magnesium nitride*, Mg_3N_2 .

Magnesium will also burn in steam, in carbon dioxide, and in sulphur dioxide:

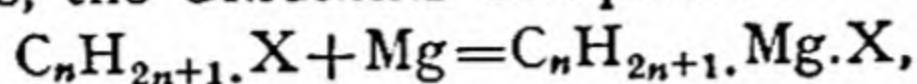


Reference to the electrochemical series (p. 246) indicates that magnesium should attack cold water vigorously: such attack is prevented by the formation of a protective film of magnesium hydroxide, $\text{Mg}(\text{OH})_2$, which is almost insoluble in water. Since the product of its action, magnesium methoxide, $\text{Mg}(\text{OCH}_3)_2$, is soluble in methyl alcohol, this reagent corrodes the metal far more rapidly than water. Magnesium combines energetically with sulphur when the two are heated together, forming MgS , and with the halogens, forming the corresponding halide. Magnesium dissolves readily in dilute acids:



but is unattacked by alkalis.

Dry magnesium with dry alkyl halides forms the well-known synthetic reagents, the GRIGNARD compounds:



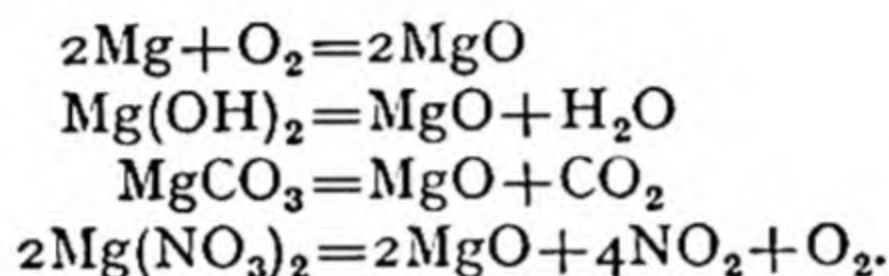
where $\text{X} = \text{Cl}, \text{Br. or I.}$

Uses. A mixture of magnesium powder and potassium perchlorate (the chlorate is dangerous) is used as a flashlight powder, but the principal use of the metal is in removing oxygen and sulphur from other metals. It is also an ingredient of many important alloys, e.g. magnalium (p. 384). These alloys are light, strong, and easily worked and are particularly adapted to aircraft construction.

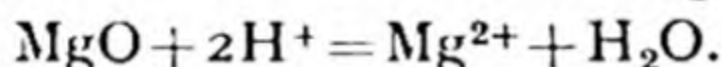
COMPOUNDS OF MAGNESIUM

Magnesium forms the colourless ion Mg^{2+} .

Magnesium oxide, magnesia, MgO , can be obtained by any of the usual methods, e.g. combustion of the metal in oxygen, and ignition of the hydroxide, carbonate, or nitrate:

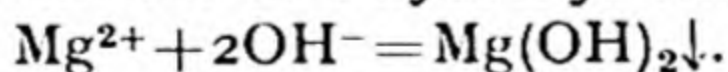


It is a white solid with a very high melting-point (nearly $3,000^\circ$) and is used as a refractory lining for high-temperature furnaces. It dissolves slightly in water, forming the hydroxide. As a basic oxide, it dissolves in dilute acids to form magnesium salts:



Old specimens may effervesce with a dilute acid, having absorbed atmospheric carbon dioxide and become converted in part into carbonate.

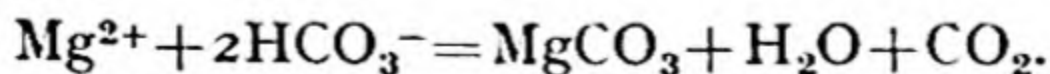
Magnesium hydroxide, $\text{Mg}(\text{OH})_2$, is very sparingly soluble in water and is therefore obtained as a white precipitate when solutions containing magnesium ions and hydroxyl ions are mixed:



The precipitation of the hydroxide by ammonia solution is prevented if much ammonium chloride is present, since the hydroxyl ion concentration is then too low (cf. p. 237).

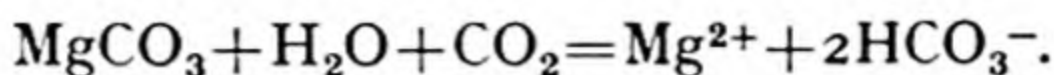
Magnesium hydroxide will not dissolve in caustic alkali solutions.

Magnesium carbonate, MgCO_3 , can be precipitated as a white powder by adding sodium bicarbonate solution to a solution of a magnesium salt:



Sodium carbonate precipitates a basic carbonate (*magnesia alba*).

If magnesium carbonate is suspended in water and a current of carbon dioxide blown through the suspension, the soluble bicarbonate is formed:

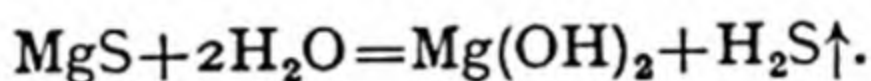


Magnesium bicarbonate is a cause of temporary hardness in water (p. 500).

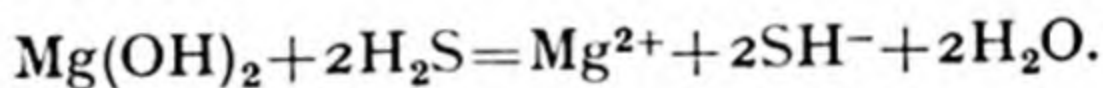
Magnesium carbonate has too high a solubility product (10^{-4}) to be precipitated in the calcium group in qualitative analysis.

Magnesium sulphate, MgSO_4 , occurs in the Stassfurt deposits as *kieserite*, $\text{MgSO}_4 \cdot \text{H}_2\text{O}$, and can be made by any of the usual methods. On cooling its aqueous solution, colourless crystals of the *heptahydrate* (Epsom salt), $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, are formed. This is used in medicine as a purgative. When heated, the heptahydrate loses its water of crystallization but undergoes no further change.

Magnesium sulphide, MgS , is made by heating the two elements together. It is entirely decomposed by water:

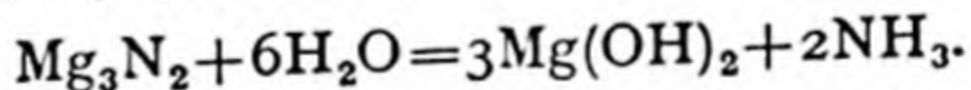


In the cold, part of the magnesium hydroxide may go into solution as the hydrosulphide:



Magnesium nitrate, $\text{Mg}(\text{NO}_3)_2$, is unknown in the anhydrous state, but can easily be prepared in solution by any of the common methods. The solution deposits colourless crystals of the *hexahydrate*, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, which decompose when any attempt is made to dehydrate them by heating.

Magnesium nitride, Mg_3N_2 , is a crystalline yellow solid made by heating magnesium in ammonia or in nitrogen. Water hydrolyses it to the hydroxide, with liberation of ammonia:

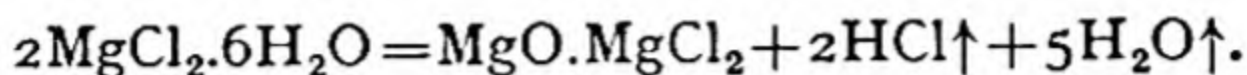


Magnesium is one of the few reagents that can be used to remove nitrogen, and was so employed in the isolation of the inert gases (p. 272).

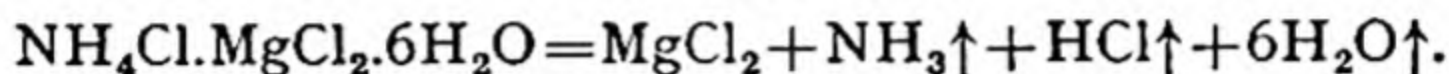
Magnesium chloride, MgCl_2 , is formed in solution when the metal, oxide, hydroxide, or carbonate is dissolved in hydrochloric acid; commercially it is obtained from carnallite (see above). From its aqueous solution it crystallizes as the colourless deliquescent *hexahydrate*, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$; traces of this occur in kitchen salt, which is therefore liable to become damp and to cake together in a moist atmosphere. (Table salt is made to run freely, even in wet weather, by mixing a little sodium phosphate with it. This converts the

magnesium chloride into the non-deliquescent magnesium phosphate; sodium chloride itself does not deliquesce. See p. 296).

When magnesium chloride hexahydrate is heated, it is partly hydrolysed, so that a residue of a basic chloride or oxychloride is left:



It may, however, be successfully dehydrated by heating it in a current of hydrogen chloride (mass-action effect), or by converting it into the double salt $\text{NH}_4\text{Cl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and heating this in the air:

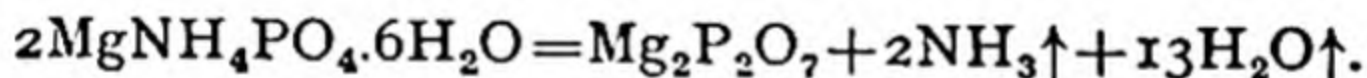


A mixture of magnesium oxide and the hexahydrate sets to a solid porcelain-like mass of the oxychloride, and is used as a dental filling and for mending broken china.

Magnesium ammonium phosphate, $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, is important in the detection and estimation of magnesium (or, conversely, of a soluble phosphate). It is formed as a white, minutely crystalline precipitate when solutions of ammonium chloride, ammonia, and ammonium phosphate are added to a solution of a magnesium salt; precipitation, which may be slow, is facilitated by scratching the inside of the vessel with a glass rod.



On ignition, magnesium ammonium phosphate loses ammonia and water, and yields a residue of *magnesium pyrophosphate*, $\text{Mg}_2\text{P}_2\text{O}_7$, which can be weighed, and the magnesium in the original compound thus estimated.



Tests for Magnesium.

1. Ignited with cobalt nitrate on the charcoal block, magnesium compounds yield a pink mass, probably a mixture of magnesium and cobaltous oxides.
2. Solutions of magnesium salts give with
 - (a) ammonia solution: white precipitate of magnesium hydroxide, $\text{Mg}(\text{OH})_2$ —but this is not precipitated if sufficient ammonium chloride is present;
 - (b) ammonia solution, ammonium chloride, and sodium dihydrogen phosphate: white precipitate (see above, $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$);
 - (c) (*spot test*) a dilute alkaline aqueous solution of paranitrobenzeneazoresorcinol: deep blue coloration.

CALCIUM, Ca

Atomic number: 20. Atomic weight: 40.08. Specific gravity: 1.53.
Melting-point: 810° . Boiling-point: $1,439^{\circ}$.

History. LAVOISIER expressed the opinion that quicklime was in reality the oxide of a metal. DAVY (1808) prepared calcium amalgam by electrolysis of a moistened mixture of lime and mercuric oxide, using a mercury cathode. By distilling off the mercury in

an inert atmosphere, he was able to obtain a residue of metallic calcium, but it was far from pure. A specimen of much higher purity was prepared in 1898 by MOISSAN, who heated calcium iodide with sodium at a high temperature.

Occurrence. Like the related elements strontium and barium, calcium is much too chemically reactive to occur naturally in the uncombined state. Calcium compounds are, however, both widespread and abundant, the chief of them being:

(i) *Calcium carbonate*, CaCO_3 , which occurs as *marble*, *limestone*, *chalk*,

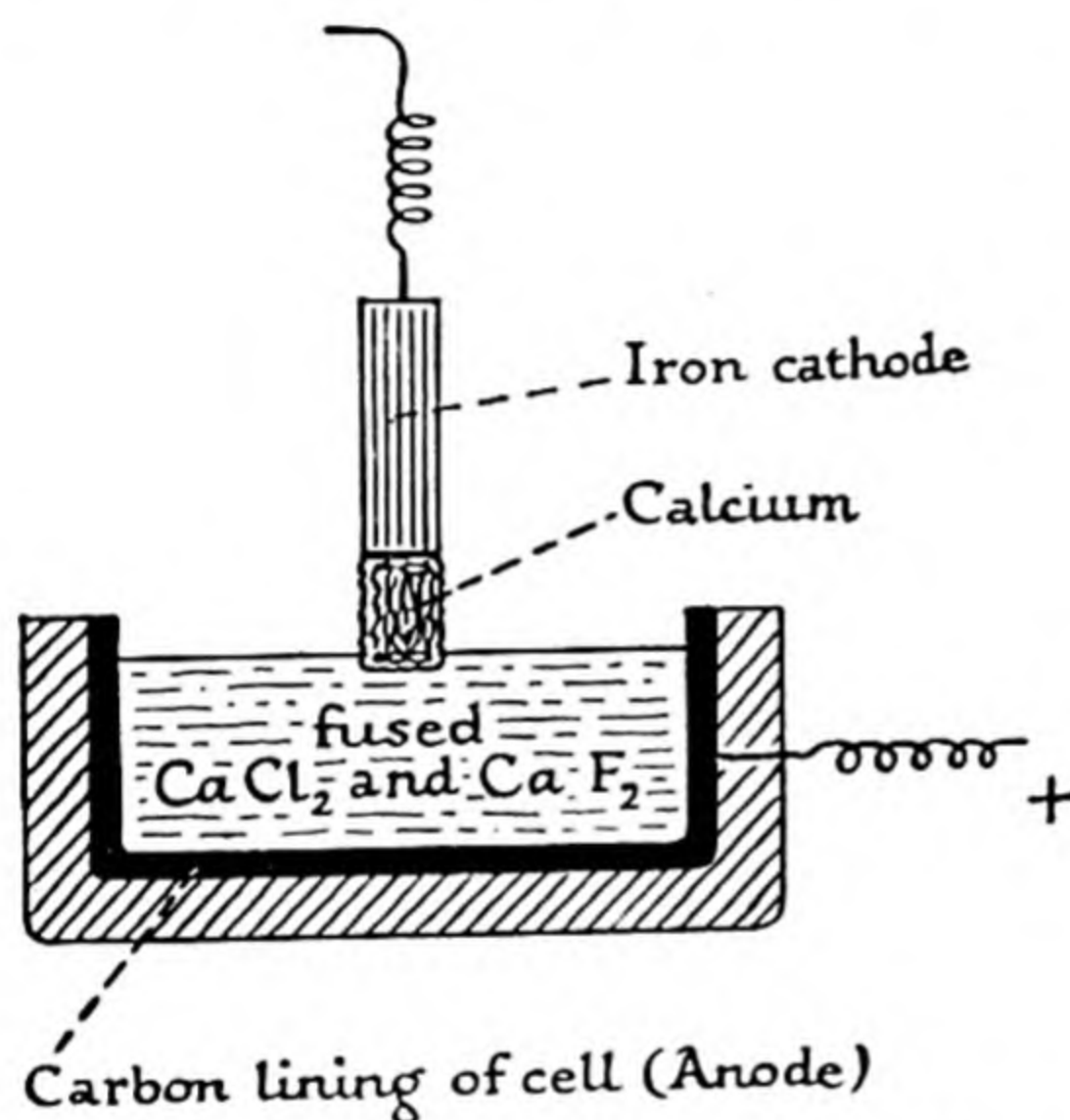


FIG. 66. PREPARATION OF CALCIUM

calcite, *aragonite*, *Iceland spar*, etc., and in combination with magnesium carbonate as *dolomite*, $\text{CaCO}_3 \cdot \text{MgCO}_3$.

(ii) *Calcium bicarbonate*, $\text{Ca}(\text{HCO}_3)_2$, which, though invisible because it exists as its aqueous solution, is nevertheless present in enormous quantities in 'the waters that cover the earth.'

(iii) *Calcium sulphate*, CaSO_4 , which is found in the anhydrous state as the mineral *anhydrite* and as the dihydrate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, in *gypsum*, *selenite*, and *alabaster*.

(iv) *Calcium phosphate*, $\text{Ca}_3(\text{PO}_4)_2$, or *phosphorite*, of which vast deposits are found in Florida (United States), North Africa, and other localities.

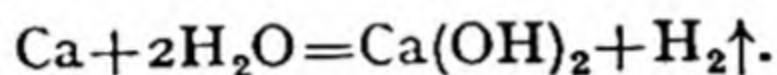
(v) *Calcium fluoride*, CaF_2 , which occurs as the mineral *fluorspar*

(bluish specimens are known as *Blue John*), and, in combination with calcium phosphate, as *apatite*, $\text{CaF}_2 \cdot 3\text{Ca}_3(\text{PO}_4)_2$.

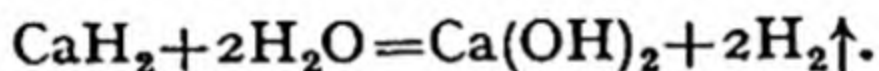
Calcium is an essential constituent of all living matter. It is found particularly in bones, teeth, blood, coral, egg-shells, and mollusc shells.

Preparation. Metallic calcium is prepared by the electrolysis of fused calcium chloride, mixed with about one-sixth of its weight of calcium fluoride to lower the temperature of fusion to about 650° . The cathode is made of an iron rod, which dips just below the surface of the molten mass, and is gradually raised as the solid calcium (M.P. 810°) is deposited upon it. In this way, a rod of the metal is at length formed, a film of the solidified electrolyte surrounding it and protecting it from corrosion by air or by the chlorine set free at the anode.

Properties. Calcium is a rather hard metal with a silvery lustre; it melts at 810° , boils at $1,439^\circ$, and has a specific gravity of 1.53. It is very chemically active, and decomposes water even in the cold:



When heated in the air, it takes fire and burns with a brilliant red flame, forming *calcium oxide*, CaO , and a little *calcium nitride*, Ca_3N_2 . It also combines with hydrogen when heated in the gas, forming *calcium hydride*, CaH_2 ; this substance, under the trade name of 'hydrolith,' is sometimes employed as a source of hydrogen, which it liberates on addition of water:



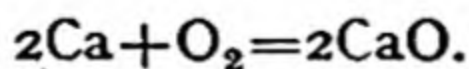
Calcium cannot be obtained by heating its oxide with carbon, since calcium and carbon unite at high temperatures to form *calcium carbide*, CaC_2 .

Metallic calcium is used as a drying agent (e.g. in the dehydration of alcohol), as a de-oxidizer, and as a constituent of certain alloys.

COMPOUNDS OF CALCIUM

Calcium is bivalent, and forms the colourless ion Ca^{2+} .

Calcium oxide, or **quicklime**, CaO , is obtained when the metal is burned in oxygen; combustion in air yields oxide and *nitride* (see above):



Industrially, quicklime is manufactured by strongly heating limestone in limekilns (preferably gas-fired):

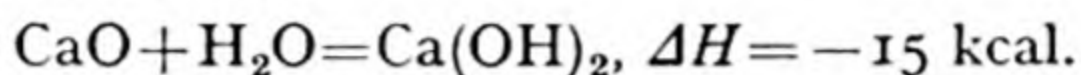


Quicklime is familiar in the form of hard, white, porous lumps.

It is very refractory, but can be melted at $2,572^{\circ}$ in the oxy-acetylene or atomic hydrogen flame. The oxy-coal-gas flame renders it incandescent, when it emits a vivid white light, formerly used for illuminating purposes as the 'limelight.'

On exposure to air, quicklime absorbs moisture and carbon dioxide, gradually falling to a powder consisting of calcium hydroxide, $\text{Ca}(\text{OH})_2$, and calcium carbonate, CaCO_3 .

When water is poured on to quicklime, a great deal of heat is given out, and the lumps again crumble to a powder, this time of calcium hydroxide alone:



This process is known as the slaking of lime and the product as slaked lime (colloquially, 'slack' lime). According to the speed with which slaking takes place, quicklime is classified by dealers as 'fat' or 'poor.' Quicklime made from pure limestone slakes quickly, and is 'fat,' but if the limestone contains clay and is heated to too high a temperature, calcium silicate is formed and clogs the pores of the quicklime so that water cannot readily percolate into the interior. Such quicklime is 'poor' and takes a long time to slake.

Calcium oxide is strongly basic, neutralizing acids to form the corresponding calcium salts and water. It is used in the laboratory as a cheap alkali, e.g. in the preparation of ammonia, and as a drying agent for alcohols and organic bases (aniline, etc.). Industrially it finds many uses, particularly in the building trade.

Mortar is a mixture of lime, water, and sand; it is made as required, and gradually sets hard by loss of moisture, and by absorption of atmospheric carbon dioxide, which converts the calcium hydroxide into calcium carbonate. It was formerly thought that some reaction between the calcium oxide and sand (SiO_2) occurred, yielding calcium silicate, but recent research has shown that this is not so.

Cement is a mixture of calcium silicates and aluminates made by strongly heating a mixture of limestone and clay. When it is mixed with water it gradually sets, possibly owing to the formation of a colloidal gel (p. 261) which becomes dehydrated and so hardens.

Soda-lime is a mixture of sodium hydroxide and calcium oxide and hydroxide. It is made either by adding molten caustic soda to lime, or by slaking quicklime with caustic soda solution and heating to evaporate the water. It has two advantages over sodium hydroxide, for which it is often used as a substitute: (a) it is not deliquescent, (b) it fuses at a much higher temperature.

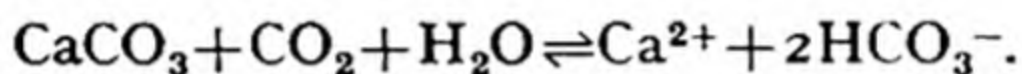
Calcium hydroxide, or **slaked lime**, $\text{Ca}(\text{OH})_2$, is a white powder, apparently amorphous but perhaps micro-crystalline; it is sparingly

soluble in water, but the solubility decreases with rise of temperature (1.85 gm. per litre at 0°, 0.77 gm. per litre at 100°). The solution is known as *lime-water*. Lime-water in which an excess of calcium hydroxide is suspended is called *milk of lime*; it is used as a whitewash.

Both quicklime and slaked lime are used in agriculture to keep down the hydrogen-ion concentration of the soil and to improve the tilth (i.e. the way the soil turns up with the plough). Lime is not a fertilizer: 'Too much lime and too little manure make both the land and the farmer poor.'

Calcium carbonate, CaCO_3 , occurs abundantly as limestone, chalk, and marble, and in smaller quantities as calcite, aragonite, and the doubly refracting Iceland spar. A chalk bed is an accretion of the shells or skeletons of countless myriads of minute sea organisms, while limestone may have been formed from chalk by the action upon it of the earth's heat under conditions in which the dissociation $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$ was not possible.

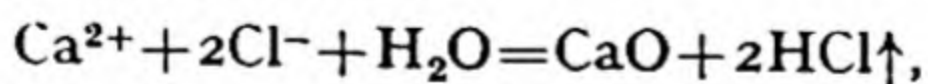
Calcium carbonate is only very slightly soluble in pure water (0.010 gm. per litre at room temperature), but dissolves slowly in water containing carbon dioxide, which converts it into the soluble bicarbonate:



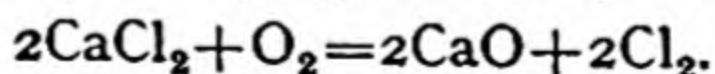
This fact is of basic importance in connection with the temporary hardness of water (p. 500).

Calcium chloride, CaCl_2 , is notorious in chemical industry as the intractable by-product of the Solvay process (p. 293). To find a profitable large-scale use for it has taxed chemical enterprise.

Since it is so cheap, there is, of course, no need to prepare it in the laboratory; but it could be made, if necessary, by any of the usual reactions, such as dissolving calcium carbonate in dilute hydrochloric acid. It is an extremely soluble salt, and deliquesces in the air. From its aqueous solution, on evaporation, colourless crystals of the hexahydrate, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, separate out. This, like the anhydrous salt, is very deliquescent. It loses its water of hydration on heating, but the anhydrous salt so obtained is contaminated with a little oxide, owing to slight hydrolysis or perhaps to reaction with oxygen in the air:



or



Hence, before calcium chloride is used for absorbing the water in a combustion, carbon dioxide should be passed through it to convert the oxide into carbonate.

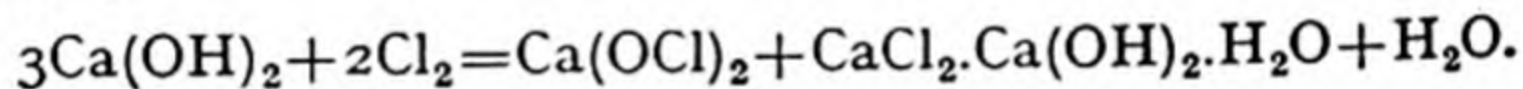
Calcium chloride is used as a drying agent (e.g. in desiccators); it

must not, however, be used for drying ammonia, amines, or alcohols, since it combines with them to form addition products such as $\text{CaCl}_2 \cdot 8\text{NH}_3$ and $\text{CaCl}_2 \cdot 4\text{CH}_3\text{OH}$.

Anhydrous calcium chloride dissolves in water with evolution of heat, but the *hexahydrate* dissolves with absorption of heat.

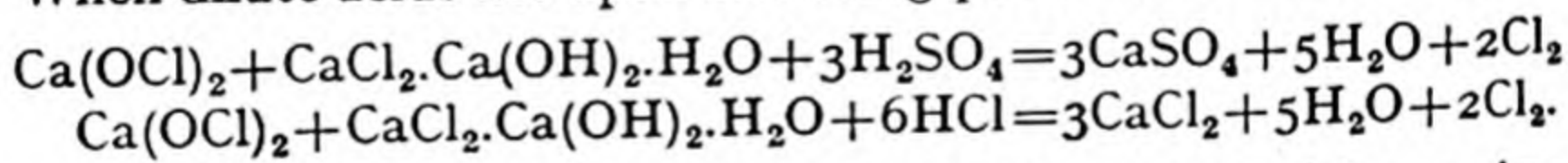
Bleaching-powder is a rather dirty white powder made by the action of chlorine upon *nearly dry* slaked lime (the proportion of moisture is not allowed to exceed 4 per cent). In BACHMANN's process the slaked lime is blown to the top of a chlorinating tower by means of compressed air, and is distributed to the highest floor of the tower through a hopper. It then falls to successive lower floors, on each of which it is mechanically raked, while a current of chlorine is driven up the tower in the opposite direction. Conditions are so adjusted that by the time the product reaches the last floor it is fully chlorinated. Hot air is now blown through it to remove free chlorine, and the bleaching-powder falls into a hopper from which it can be delivered into containers.

Bleaching-powder ('chloride of lime'), on analysis by modern methods of X-ray diffraction, proves to be a mixture of *calcium hypochlorite*, $\text{Ca}(\text{OCl})_2$, with *basic calcium chloride monohydrate*, $\text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \cdot \text{H}_2\text{O}$. Its formation may be represented by the equation:



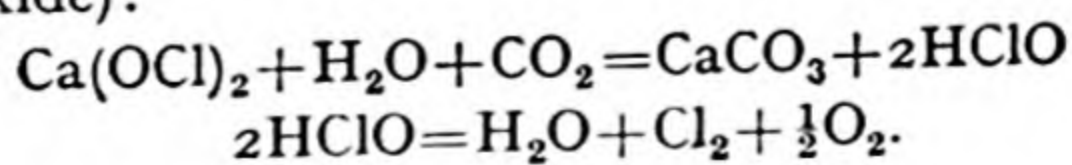
The main reaction is, however, accompanied by side-reactions, so that impurities are always present. These include calcium chlorate, $\text{Ca}(\text{ClO}_3)_2$, and calcium chloride tetrahydrate, $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$, as well as some unchanged slaked lime.

When dilute acids act upon bleaching-powder, chlorine is evolved:

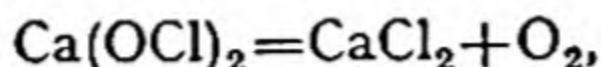


A calculation will show that a mixture of the composition assigned to bleaching-powder should liberate 41 per cent of its weight of chlorine, and this is the approximate actual yield from a very good specimen. The ordinary commercial product contains 36-40 per cent of such 'available' chlorine, i.e. chlorine set free by the action of a dilute acid. If the lime is insufficiently chlorinated, the product naturally contains a lower percentage of available chlorine.

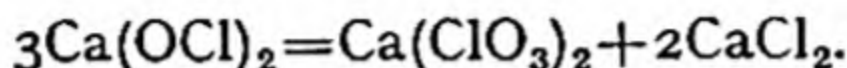
On exposure to air, bleaching-powder gradually loses chlorine, owing to the action of carbonic acid (atmospheric moisture and carbon dioxide):



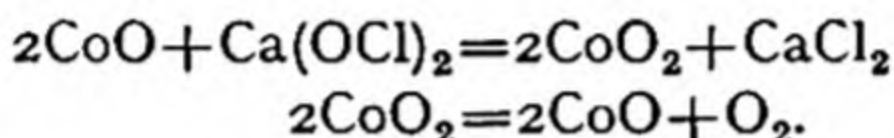
It should therefore be preserved in air-tight tins or bottles; but even so it slowly deteriorates, partly by loss of oxygen from the hypochlorite:



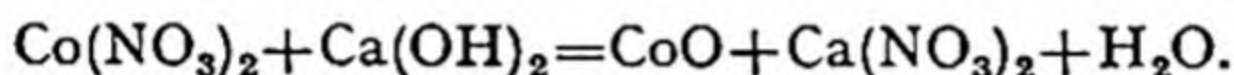
and partly by disproportionation of the hypochlorite into chlorate and chloride:



The decomposition of the hypochlorite into chloride and oxygen is catalysed by cobalt oxide. If a suspension of bleaching-powder is heated with a little cobalt nitrate solution a vigorous evolution of oxygen occurs. It is thought that the mechanism of this catalysis may be the alternate formation and decomposition of cobalt peroxide:

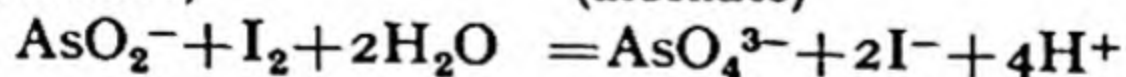
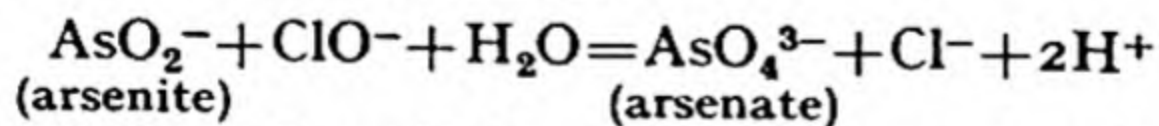


The original cobaltous oxide, CoO , is formed by the action of the lime in the bleaching-powder:



A fabric to be bleached is steeped in a dilute solution of bleaching-powder and then exposed to the air for some time. Atmospheric 'carbonic acid' liberates hypochlorous acid, HClO , from the bleaching-powder, and this destroys the colouring-matter (p. 553). The fabric is then rinsed in water acidified with a little sulphuric acid, to decompose any unchanged bleaching-powder, and is afterwards placed in an antichlor bath (p. 536). Finally it is thoroughly washed in water.

The hypochlorite and therefore the available chlorine in bleaching powder may be estimated by mixing a weighed sample with excess of standard sodium arsenite solution, and then titrating the remaining arsenite with iodine solution:



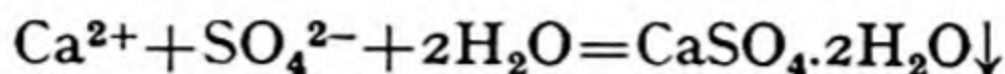
1 litre of N/10 arsenite \equiv 3.55 gm. of available chlorine.

Owing to its strong oxidizing power, bleaching-powder is a good germicide and is widely used as a disinfectant.

Calcium sulphate, CaSO_4 , occurs native as *anhydrite*, CaSO_4 , and in the form of the dihydrate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, as *gypsum* (opaque), *selenite* (transparent), and *alabaster* (translucent). It is only slightly soluble in water—about 2 gm. per litre at room temperature—and

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may therefore be obtained by precipitation. The precipitate consists of the dihydrate, not the anhydrous salt:

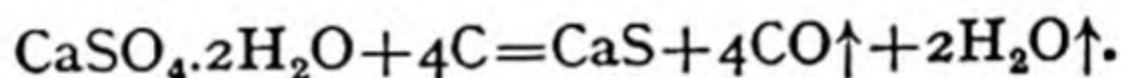


Calcium sulphate is a cause of permanent hardness in water (p. 500). It is soluble in concentrated ammonium sulphate solution.

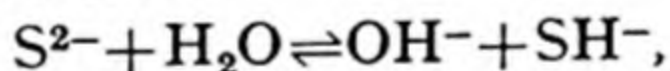
When gypsum is heated to 110° – 130° , it loses three-quarters of its water of crystallization and is converted into the hemihydrate, $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ or $(\text{CaSO}_4)_2 \cdot \text{H}_2\text{O}$. This is used as a plaster, and since it was first made on a large scale at Montmartre, a district of Paris once popular with artists, it is known as *plaster of Paris*. When mixed with water, it is rapidly reconverted into gypsum, and the mass sets solid. Slight expansion occurs on setting, and the plaster cast thus faithfully reproduces the details of the mould. If gypsum is heated to above 200° ('dead-burnt'), the whole of the water of crystallization is driven off, and the anhydrous salt is left. This sets extremely slowly.

In its precipitated form, gypsum is used as a 'filler' for glazed paper, e.g. that upon which half-tone plates are printed.

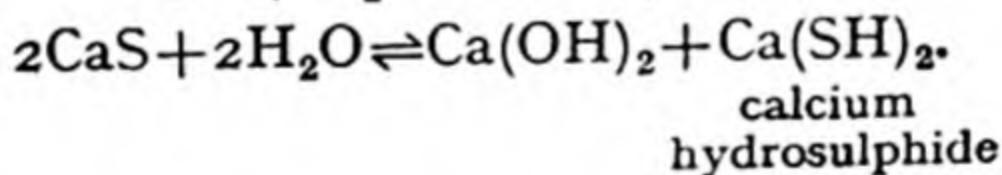
Calcium sulphide, CaS , is made by heating gypsum with powdered coke:



It is a white solid, slightly soluble in water but partially converted into hydrosulphide in solution:



or



Impure specimens of calcium sulphide (and barium sulphide) often shine in the dark after exposure to sunlight.

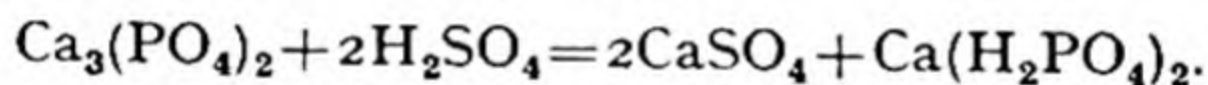
Calcium bisulphite, $\text{Ca}(\text{HSO}_3)_2$, is made by passing sulphur dioxide into milk of lime until no further absorption of the gas occurs. It is used in making lower-grade paper (e.g. newspaper) from wood; best-quality paper is made from rags. Wood consists mainly of two substances, lignin and cellulose, the second of which is required for the paper-making. By steeping wood chips in hot calcium bisulphite solution under pressure, the lignin is dissolved, but the cellulose is left unattacked.

Calcium nitrate, $\text{Ca}(\text{NO}_3)_2$, crystallizes from aqueous solution as the colourless, deliquescent tetrahydrate, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. A basic nitrate, which is not deliquescent, and is therefore better for transport, storage, and application, is used for an artificial manure

('Norwegian saltpetre'—*not* 'nitrochalk,' which is a mixture of chalk and ammonium nitrate (p. 451).

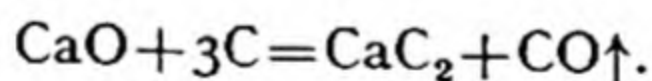
Calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, is a white solid only slightly soluble in water but readily soluble in dilute acids (cf. p. 238). It is an extremely valuable fertilizer, since phosphorus is an essential element in the mineral food of plants, and the average soil contains far less phosphate than the optimum for plant growth. The rocky form (*phosphorite*, p. 338) in which calcium phosphate occurs naturally in Florida and North Africa is, however, practically insoluble in water unless very finely ground; hence it must be reduced to this condition before application to the land.

An alternative method of rendering the phosphate available—a method still largely used, but declining since the introduction of efficient machinery for grinding the phosphorite to the required degree of fineness—is to convert the calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, into calcium hydrogen phosphate, $\text{Ca}(\text{H}_2\text{PO}_4)_2$, which is soluble in water. The finely ground phosphorite is mixed with about its own weight of 65 per cent sulphuric acid and the mixture is agitated in rotary metal autoclaves, under a pressure of 6 atmospheres. The product is obtained in the form of granules ready for marketing; it consists of a mixture of $\text{Ca}(\text{H}_2\text{PO}_4)_2$ with calcium sulphate, and is known commercially as 'superphosphate':

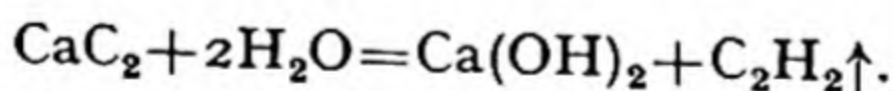


The manufacture of superphosphate accounts for about two-fifths of the total annual consumption of sulphuric acid.

Calcium carbide, CaC_2 , is a highly important industrial chemical made by strongly heating a mixture of quicklime and carbon (coke) in the electric furnace:

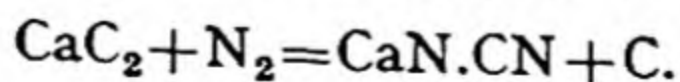


When pure, it is a colourless crystalline solid, but the commercial substance forms hard greyish lumps. On addition of water it yields acetylene:



From acetylene are manufactured acetaldehyde, CH_3CHO , acetic acid, CH_3COOH , and a wide variety of other organic compounds. In recent years, a whole 'acetylene chemistry' has been developed; it has proved most valuable in elucidating the structure of carotenes and various vitamins.

Calcium cyanamide, CaN.CN , is a useful artificial manure made by heating calcium carbide to about $1,000^\circ$ in a current of nitrogen:



Tests for Calcium.

1. Calcium compounds colour the flame orange-red.
2. Calcium ions, Ca^{2+} , give with
 - (a) ammonium carbonate: white precipitate of calcium carbonate;
 - (b) ammonium oxalate: white precipitate of calcium oxalate, CaC_2O_4 ; *
 - (c) a saturated solution of calcium sulphate: no precipitate (distinction from barium and strontium).

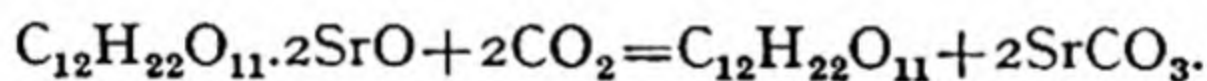
* This reaction may be used in the gravimetric estimation of calcium. The oxalate is ignited and weighed as oxide.

STRONTIUM, Sr

Atomic number: 38. *Atomic weight:* 87.63. *Specific gravity:* 2.5.
Melting-point: 752°. *Boiling-point,* 1,366°.

Strontium. Strontium occurs naturally as the carbonate (SrCO_3), *strontianite* (so called because it was first discovered at Strontian, Argyllshire), and also as the sulphate, *celestine*, SrSO_4 . It can be obtained by the electrolysis of its fused chloride, and is a white metal very similar to calcium and barium.

Strontium Compounds. The resemblance between the elements calcium, strontium, and barium extends to their compounds. On the whole, strontium compounds resemble those of calcium more than those of barium. *Strontium hydroxide*, $\text{Sr}(\text{OH})_2$, is used in the refinement of sucrose (cane-sugar), with which it forms an insoluble compound, said to be $\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot 2\text{SrO}$. This is filtered off from the sucrose mother-liquor (molasses), and washed, after which it is stirred up in water and decomposed by means of a current of carbon dioxide.



The carbonate is removed by filtration and the oxide recovered by heating. The similar calcium compound is too soluble to be used in this way, and the barium compound is violently poisonous. *Strontium nitrate*, $\text{Sr}(\text{NO}_3)_2$, is used in the firework industry for producing red flares. All volatile strontium compounds colour the Bunsen flame a beautiful and brilliant crimson.

BARIUM, Ba

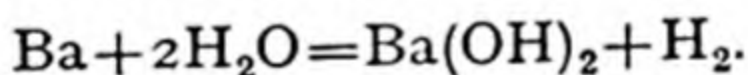
Atomic number: 56. *Atomic weight:* 137.36. *Specific gravity:* 3.8.
Melting-point: 830°. *Boiling-point:* 1,737°.

History. VINCENZO CASCIOLO of Bologna, in 1602-3, observed that the mineral heavy spar (BaSO_4), when heated strongly with charcoal, yielded a substance that glowed in the dark after exposure to light. This substance (impure barium sulphide, BaS) was known as the 'Bolognan stone' or 'Bolognan phosphorus.' The impure metal was first obtained in 1808 by DAVY, who electrolysed the fused chloride. The name *barium* is derived from the Greek *barys*, 'heavy,' and refers to the high density of barium sulphate.

Occurrence. Barium does not occur in nature as the free element, but is comparatively abundant as *heavy spar* or *barytes*, BaSO_4 , and as *witherite*, BaCO_3 .

Extraction. Barium can be prepared by the electrolysis of an aqueous solution of barium chloride, using a mercury cathode. The barium forms an amalgam with the mercury; this is dried, and heated in an inert atmosphere, when the mercury distils off and leaves a residue of metallic barium.

Properties. Barium is a silvery-white, rather hard metal of great chemical activity. It readily oxidizes in the air, and burns with a brilliant greenish flame when heated in air or oxygen. It liberates hydrogen from water in the cold:

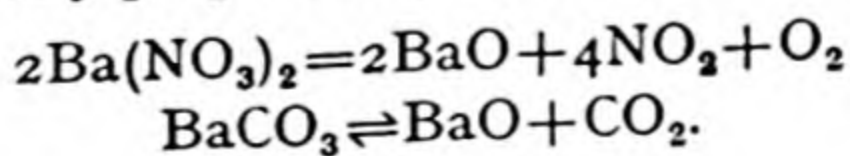


Barium salts are poisonous (when soluble), and colour the Bunsen flame apple-green. They are made from the carbonate by the action of dilute acids, and from the sulphate in one of two ways: (i) by fusion with an excess of sodium carbonate to give the carbonate, which is insoluble in water and can therefore be obtained by extracting the mass with water to remove the sodium sulphate and residual sodium carbonate— $\text{BaSO}_4 + \text{Na}_2\text{CO}_3 = \text{BaCO}_3 + \text{Na}_2\text{SO}_4$; (ii) by strongly heating with carbon to form the sulphide, which is then dissolved in the appropriate acid— $\text{BaSO}_4 + 4\text{C} = \text{BaS} + 4\text{CO}\uparrow$.

COMPOUNDS OF BARIUM

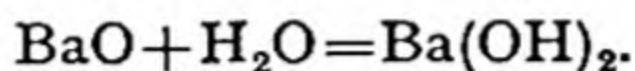
Barium forms the colourless ion Ba^{2+} .

Barium oxide, BaO , can be obtained by burning the metal in oxygen, but is usually prepared by heating the nitrate or carbonate:

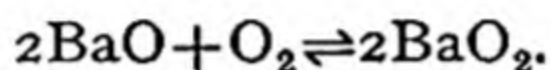


In the last reaction, the addition of carbon is advantageous, since the decomposition of the carbonate requires a high temperature; carbon removes carbon dioxide as carbon monoxide and so assists the left-to-right change.

Barium oxide is a white, difficultly fusible solid resembling calcium oxide. It is a basic oxide, and unites energetically with water to form the hydroxide:

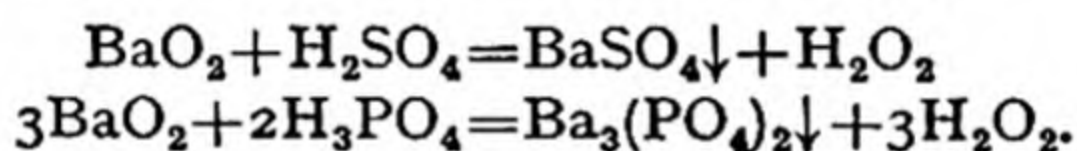


On heating in air or oxygen, barium oxide is converted into barium peroxide (at about 500° in air, and at a rather lower temperature in oxygen). On raising the temperature further by some 200° , the reverse change takes place, and oxygen is given off:



This reversible process was formerly used in the industrial preparation of oxygen from the atmosphere (BRIN's process).

Barium peroxide, BaO_2 , prepared in the manner just described, is a white powder which, on addition to cold dilute sulphuric acid or phosphoric acid, yields hydrogen peroxide (q.v.):

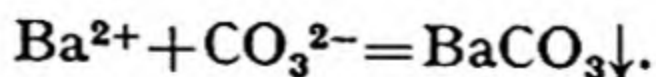


By the action of hydrogen peroxide on a solution of barium hydroxide, the peroxide may be obtained in the octahydrated form, $\text{BaO}_2 \cdot 8\text{H}_2\text{O}$.

Barium hydroxide, Ba(OH)_2 , is formed when water is added to the oxide. It is about ten times as soluble in water as calcium hydroxide, at room temperature, and its solubility, unlike that of Ca(OH)_2 , increases with rise of temperature. From aqueous solution it crystallizes out as the octahydrate, $\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$. It is a strongly basic substance, and is used in volumetric analysis for making a standard alkali solution: 'baryta water' has the advantage over sodium and potassium hydroxide solutions of never containing any dissolved carbonate, since barium carbonate is insoluble.

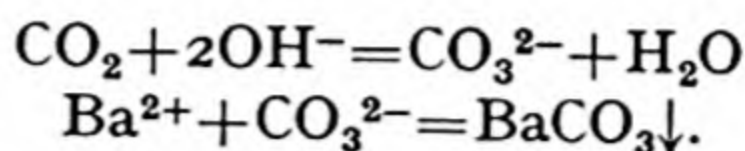
On strong heating, barium hydroxide loses water and is converted into the oxide, but the reaction requires a temperature of 900° – $1,000^\circ$ to take place at all quickly.

Barium carbonate, BaCO_3 , is formed as a white precipitate when sodium carbonate solution is added to a solution of a barium salt:

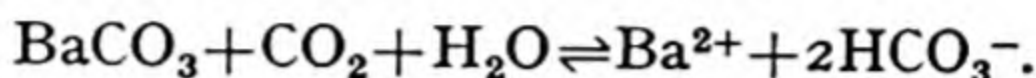


350 MAGNESIUM, CALCIUM, STRONTIUM, BARIUM

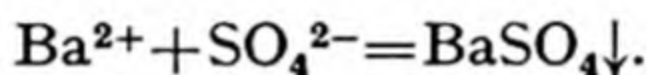
It is also precipitated when carbon dioxide is passed into baryta water:



On further passage of carbon dioxide, the barium carbonate slowly dissolves, forming the bicarbonate:

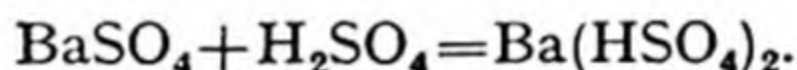


Barium chloride, BaCl_2 , is obtained by dissolving the oxide or carbonate in dilute hydrochloric acid and concentrating the solution by evaporation. It crystallizes from aqueous solution as the colourless, non-deliquescent dihydrate, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, which yields the anhydrous salt on heating. Barium chloride is used for the detection and estimation of sulphate ions, with which it gives a white precipitate of barium sulphate; this can be collected, washed, dried, and weighed:



Barium nitrate, $\text{Ba}(\text{NO}_3)_2$, is a colourless *anhydrous* crystalline solid, used in pyrotechny for making green flares.

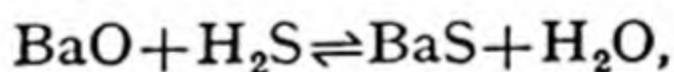
Barium sulphate, BaSO_4 , is a very insoluble compound formed when barium ions and sulphate ions meet. It will dissolve fairly easily in hot concentrated sulphuric acid, owing to the formation of the hydrogen sulphate:



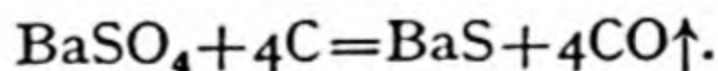
Medicinally it finds application in X-ray work, since it is opaque to X-rays, and non-poisonous (being insoluble). It is fed to patients of whose alimentary system an X-ray photograph is to be taken.

For the use of barium sulphate in *lithopone*, see p. 358.

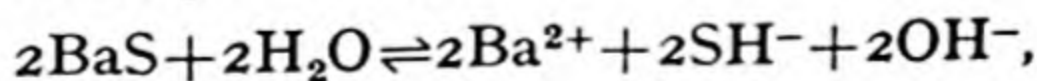
Barium sulphide, BaS , is made by heating barium oxide in a current of hydrogen sulphide:



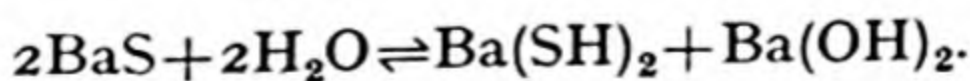
or—more usually—by heating a mixture of barium sulphate and carbon:



It is only very slightly soluble in cold water, but goes into solution readily on heating, owing to conversion into the easily soluble hydrosulphide and hydroxide:

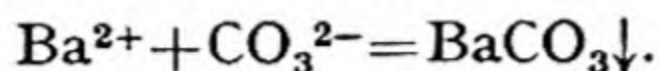


or:

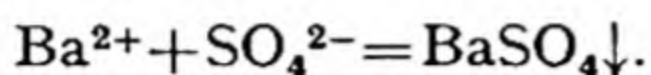


Tests for Barium.

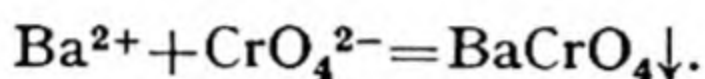
1. Apple-green flame (platinum wire difficult to clean afterwards).
2. Ammonium carbonate in neutral or alkaline solution gives a white precipitate of barium carbonate:



3. A solution containing SO_4^{2-} ions gives a white precipitate of barium sulphate:



4. Potassium chromate in neutral solution gives a yellow precipitate of barium chromate, insoluble in acetic acid but soluble in mineral acids:



5. (*Spot test.*) Sodium rhodizonate * solution (1 part per 1,000 of water) gives a reddish-brown precipitate of barium rhodizonate. This is insoluble in dilute hydrochloric acid (distinction from strontium). The test is exceedingly sensitive.

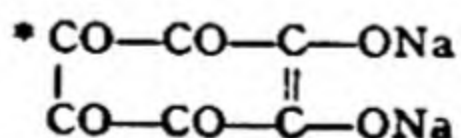
COMPARATIVE EXERCISES

1. Draw up the usual kind of table (cf. pp. 310 and 332) for calcium, strontium, and barium. Note, among other points, the solubility of their hydroxides; the formation of hydrides; action of the metals on water; behaviour of nitrates, carbonates, etc., on heating.

2. Make a list of any important differences you can discover between calcium, strontium, and barium.

3. Make similar lists to the above for magnesium and calcium.

4. After reading Chapter XXV, compare and contrast the properties of (a) magnesium and zinc, (b) zinc and calcium.



CHAPTER XXV

GROUP II

ZINC, CADMIUM, MERCURY

Beryllium—Magnesium $\left\{ \begin{array}{l} \text{[Calcium—Strontium—Barium—Radium]} \\ \text{Zinc—Cadmium—Mercury} \end{array} \right.$

ZINC, Zn.

Atomic number: 30. *Atomic weight:* 65.38. *Specific gravity:* 7.13.
Melting-point: 419°. *Boiling-point:* 907°.

History. Though brass—an alloy of zinc and copper—was known at least a thousand years before the Christian era, the term *zinc*, as the name of a distinct metal, seems to have been first employed by PARACELSUS (1493–1541). In his *Book of Minerals* he says that ‘there is another metal, *zinckum*, which is in general unknown to the [chemical] fraternity,’ but admits that he is still unfamiliar with its real nature. There is reason to believe that zinc had been prepared in China for several centuries before this, and it is mentioned as an import from that country by a Moslem writer of about A.D. 1300. A zinc mine at Shui-Ko-Shan, in the province of Hunan, has been worked for the last three hundred years. The Persian word for zinc was *safid-ruy*, or ‘white copper,’ whence our name for the commercial metal, viz. ‘spelter.’ HENCKEL (1720) prepared metallic zinc comparatively free from impurities, and in 1740 a works for extracting it from calamine (ZnCO_3) was established by CHAMPION at Bristol—a city where zinc-smelting is still an important local industry.

Occurrence. Zinc is an abundant and widely distributed element, most countries having workable deposits of zinc minerals. The chief ores are *zinc blende*, ZnS ; *calamine* or *zinc spar*, ZnCO_3 ; and *hemimorphite*, a hydrated silicate of zinc with the composition $\text{Zn}_2\text{SiO}_4 \cdot \text{H}_2\text{O}$. The United States, Belgium, Germany, Poland, and Australia (New South Wales) are the largest producers. The annual world output of the metal is so great that it was for a time limited by mutual agreement among some of the firms concerned.

Extraction. Zinc blende or sphalerite, the chief ore of zinc, is almost always found in association with galena, PbS (p. 418). The ore is first finely crushed and then separated from gangue (earthy impurities) and the galena by a process of differential flotation; this consists in mixing the powdered ore with water and oil and blowing a current of air through the liquid. By suitably adjusting the proportions of oil and water, the frothy bubbles that rise to the surface may be made to carry the blende with them, leaving the galena and gangue behind. The blende particles are then recovered from the froth by means of a vacuum filter or in other ways.

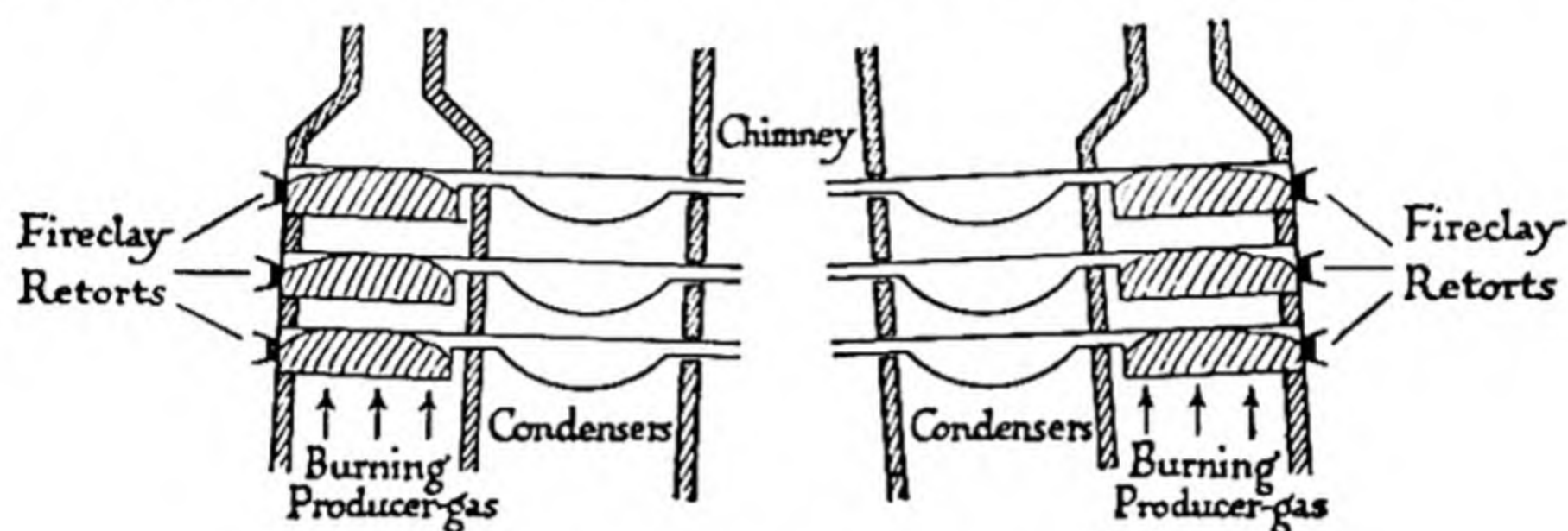
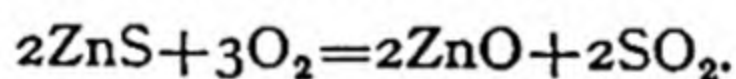
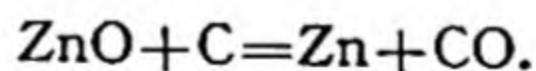


FIG. 67. ZINC DISTILLATION (DIAGRAMMATIC)

The 'zinc concentrates' are roasted in a current of air in a mechanical multiple-hearth furnace heated by producer-gas, when zinc oxide and sulphur dioxide are obtained:

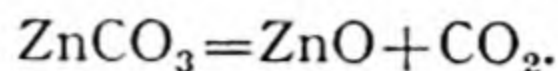


The sulphur dioxide is cleaned and used in the manufacture of sulphuric acid, while the zinc oxide is mixed with anthracite and heated at about $1,300^\circ$ in small horizontal retorts set in special furnaces; each furnace may contain as many as 380–400 retorts. Alternatively the mixture of oxide and anthracite is compressed into briquettes and passed continuously through furnaces arranged vertically:



The zinc vapour leaving the furnaces is condensed to a liquid in fire-clay or sheet-iron condensers cemented to the retorts, while the carbon monoxide passes up the chimney. The liquid zinc is run into moulds and cast in slabs. To the ends of the condensers are attached iron tubes in which a powder consisting of zinc dust and zinc oxide collects; if purer zinc dust is required, these tubes are made longer, so that all the zinc vapour has condensed before coming into contact with atmospheric oxygen.

Calamine and hemimorphite are treated in the same kind of way as zinc blende; the preliminary roasting converts the calamine into zinc oxide and serves to dehydrate the hemimorphite:



The oxide and silicate respectively are then reduced with anthracite as before.

Refinement of the crude zinc, or *spelter*, is effected by electrolysis in a slightly acid solution of zinc sulphate; lead and arsenic, the



Imperial Smelting Corporation Ltd.

FIG. 68. ZINC RETORTS IN FURNACE

chief impurities in spelter, are thus removed and the zinc is obtained in a state of very high purity (over 99.99 per cent). If required still purer it may be fractionally distilled under reduced pressure, using a still made of silicon carbide.

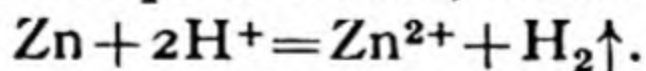
Nowadays much zinc is extracted electrolytically. The roasted sulphide ore is leached out with dilute sulphuric acid and the resulting solution of zinc sulphate is electrolysed between lead anodes and aluminium cathodes. The temperature is maintained at about 35°, and a current of 40 amperes is used. The deposits of zinc are stripped off the cathodes from time to time.

Properties. Zinc is a greyish-white metal, somewhat brittle when cold but malleable and ductile when gently warmed to 100° – 150° . At 205° it becomes brittle again, and may then be crushed to powder in an iron mortar. Spelter is fairly hard—harder than tin and silver—but pure zinc is considerably softer and silver will scratch it. Zinc melts at 419° and boils at 907° ; vapour density determinations show that the vapour is monatomic (Zn).

Zinc is very stable in dry air, but on heating takes fire at about 500° , burning with a greenish-blue flame and yielding a white cloud of zinc oxide, the so-called 'philosopher's wool.' A mass of fine zinc threads may be ignited by applying the Bunsen flame to it. In moist air, zinc is slowly tarnished by the formation of a white film of the basic carbonate; this film is coherent and protects the underlying metal from further corrosion. It is upon this property that the chief use of zinc, viz. as a protective coating for iron and steel, depends (cf. also p. 245). Zinc-coated iron is described as 'galvanized'—possibly because the deposition of a thin coat of one metal upon another is usually effected by 'galvanism,' or electricity. In making galvanized iron, however, electrolytic methods are much less extensively used than is the common procedure of dipping the thoroughly cleaned iron sheet into a bath of molten zinc containing small quantities (less than 1 per cent) of lead and tin, and removing the superfluous zinc by passing the galvanized sheet between rollers.

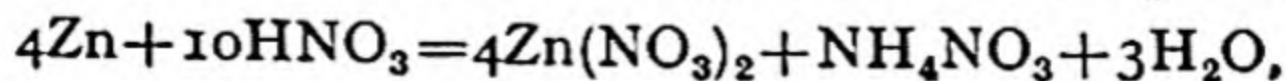
A dry method of galvanizing is known as 'sherardizing,' after its inventor, SHERARD COWPER-COLES. The clean iron objects are packed in a drum with dried zinc dust, and the drum is then heated to about 300° – 400° for some hours. The iron thus becomes coated with (a) an alloy containing a little zinc and much iron, (b) an outer alloy containing much zinc and little iron, and (c) an outermost coating of pure zinc. Sherardizing is very useful for the treatment of small articles such as screws, nuts, bolts, etc. Still another method of galvanizing iron objects is to spray them with the molten metal, while electrolytic deposition of zinc from solutions of the sulphate, chloride, and cyanide is finding increasing application.

Zinc, when slightly impure, dissolves readily in dilute hydrochloric acid and dilute sulphuric acid, liberating hydrogen:



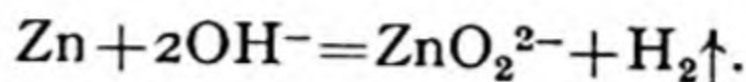
If the metal is very pure, little action occurs.

With dilute nitric acid, zinc yields zinc nitrate together with nitric oxide, nitrous oxide, and ammonium nitrate. Several reactions appear to take place simultaneously, so that the equation:



does not express the whole truth.

Concentrated nitric acid attacks zinc with vigour, clouds of nitrogen dioxide being given off. Hot concentrated sulphuric acid is reduced by zinc not merely to sulphur dioxide, but to sulphur and hydrogen sulphide. Zinc will also dissolve in caustic alkali solution (distinction from *magnesium*), yielding zincates with evolution of hydrogen:

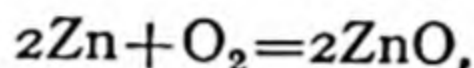


Cf. aluminium, p. 380.

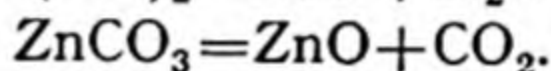
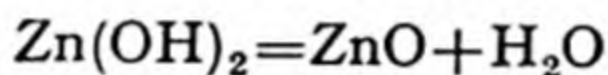
COMPOUNDS OF ZINC

Zinc forms the colourless cation Zn^{2+} .

Zinc oxide, ZnO . Zinc oxide may be obtained by burning the metal in air or oxygen:

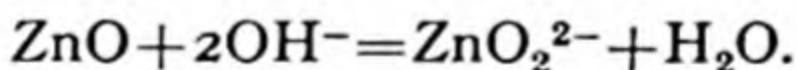


or by heating the hydroxide, carbonate, or nitrate: *



It is a white powder which becomes yellow on heating, though the white colour is restored on cooling. It can easily be reduced to zinc by heating it with carbon, but is reduced only with considerable difficulty when heated in hydrogen. It readily dissolves in dilute acids to give the corresponding zinc salts, and absorbs moisture and atmospheric carbon dioxide if left exposed to the air.

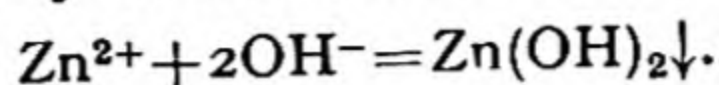
Zinc oxide is practically insoluble in water, but slowly dissolves in sodium or potassium hydroxide solution to give the corresponding zincate (see below):



Industrially zinc oxide is used as a pigment, under the name of 'zinc white' or 'Chinese white.' Its covering-power is not so great as that of white lead (q.v.), but it is not blackened by hydrogen sulphide, since zinc sulphide is itself white. When mixed with white-lead paints, zinc white produces a pigment which gives a harder and more resistant surface than the white lead alone. Pure zinc oxide is a good antiseptic, and is used in zinc ointment. Zinc oxide is also used to some extent in glass manufacture, since it renders the glass less soluble in water, hydrochloric acid, and sodium carbonate.

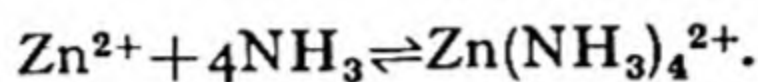
* Anhydrous zinc nitrate is apparently unknown; the decomposition by heat of the hexahydrate gives a residue of zinc oxide, but the reaction is too complex to be conveniently represented by a single equation.

Zinc hydroxide, $\text{Zn}(\text{OH})_2$, is obtained as a white precipitate when a solution of sodium hydroxide is added to a solution of a zinc salt:

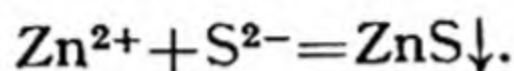


It will dissolve in dilute acids, forming the corresponding zinc salts, and is soluble in excess of caustic alkali solution, forming zincates in which the zinc constitutes part of the anion, ZnO_2^{2-} . Zinc hydroxide is thus *amphoteric*. The zincates may be obtained in the solid state by adding alcohol (in which they are insoluble) to their concentrated aqueous solution.

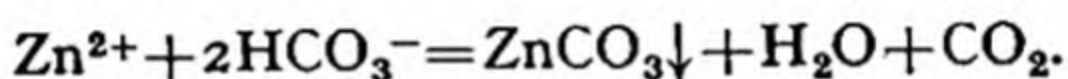
Zinc hydroxide will also dissolve in ammonia solution, again with formation of a complex ion; but in this case the complex is a *cation*, $\text{Zn}(\text{NH}_3)_4^{2+}$:



At equilibrium, a sufficiently high concentration of Zn^{2+} ions is left to give a precipitate of zinc sulphide with ammonium sulphide:



Zinc carbonate, ZnCO_3 , occurs native as calamine. It can be prepared by adding sodium bicarbonate solution to a solution containing zinc ions:



Sodium carbonate solution precipitates a mixture of the normal carbonate and a basic carbonate.

The familiar 'calamine lotion,' used to allay the discomfort of sunburn and midge-bites, is a mixture of zinc carbonate (1 gm.), zinc oxide (1 gm.), lime-water (5 c.c.), glycerol (12 c.c.), and water (30 c.c.).

Zinc chloride, ZnCl_2 , is formed when the metal, oxide, hydroxide, or carbonate is dissolved in hydrochloric acid. On concentration, the solution deposits colourless, deliquescent crystals of the monohydrate, $\text{ZnCl}_2 \cdot \text{H}_2\text{O}$. If these are heated in the air, hydrolysis occurs and basic salts, e.g. $\text{Zn}(\text{OH})\text{Cl}$ and $\text{ZnO} \cdot \text{ZnCl}_2$, are left. The anhydrous salt can, however, be obtained by heating the hydrate in a current of hydrogen chloride, or by direct synthesis from zinc and either chlorine or hydrogen chloride.

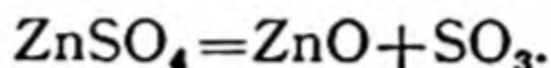
Anhydrous zinc chloride is used in organic chemistry as a dehydrating agent (e.g. in esterification) and as a catalyst. A mixture of zinc oxide with a very concentrated solution of zinc chloride quickly sets to a hard white mass and is used in dentistry as a filling.

Zinc chloride dissolves readily in alcohol, acetone, and ether. Its aqueous solution reacts acid.

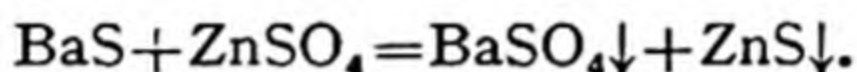
Zinc sulphate, ZnSO_4 . In the form of its *heptahydrate*,

$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, commonly known as *white vitriol*, or *zinc vitriol*, zinc sulphate may be prepared by dissolving the metal, oxide, hydroxide or carbonate in dilute sulphuric acid and concentrating the solution to the point of crystallization. On the commercial scale, it is obtained by roasting blende (p. 352) and extracting the roasted product with dilute sulphuric acid.

White vitriol is a crystalline solid isomorphous with Epsom salt (q.v.). On careful heating, it yields the anhydrous salt, ZnSO_4 , which at temperatures above 739° decomposes into zinc oxide and sulphur trioxide:



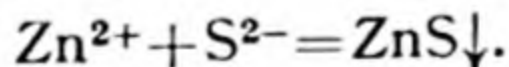
The principal use of zinc sulphate is in the manufacture of *lithopone*, a white pigment consisting of a mixture of zinc sulphide and barium sulphate ('blanc fixe'). It is prepared by running a dilute solution of zinc sulphate into a solution of barium sulphide:



The precipitate is washed, filtered, heated to a dull red heat, and quenched in cold water, the object of the last treatments being to improve the texture of the product. Lithopone is the most opaque of all white pigments, and has the additional advantage of being non-poisonous. A *cadmium lithopone*, $\text{BaSO}_4 + \text{CdS}$, made by substituting cadmium sulphate for zinc sulphate as the precipitating agent, has a rich yellow colour. Zinc lithopone is used extensively in the manufacture of linoleum and as a 'filler' in the rubber industry.

A solution of zinc sulphate and boric acid has merits as an eye lotion; a solution of zinc chloride is used for the same purpose.

Zinc sulphide, ZnS . A mixture of zinc dust and flowers of sulphur burns brightly if ignited, and inflames spontaneously if struck with a hammer. The product is zinc sulphide, which is, however, more conveniently prepared by passing hydrogen sulphide into an ammoniacal solution of a zinc salt, as in qualitative analysis; the zinc sulphide comes down as a white precipitate:



When not quite pure, and particularly when traces of copper form the impurity, zinc sulphide exhibits a beautiful greenish phosphorescence after exposure to light, or in the presence of a radioactive compound. The luminous paint used on watch and clock dials consists of zinc sulphide with a minute quantity of such a compound to excite its phosphorescence.

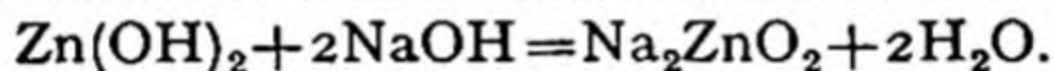
Zinc nitrate, $\text{Zn}(\text{NO}_3)_2$. From a solution of the metal, or its oxide, hydroxide, or carbonate, in nitric acid, crystals of zinc nitrate hexahydrate, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, may be obtained on concentrating and cool-

ing. They are colourless and deliquescent and are soluble in both water and alcohol. Anhydrous zinc nitrate appears to be unknown.

Zinc phosphate, $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, is obtained as a gelatinous precipitate when solutions of zinc sulphate and sodium phosphate, Na_2HPO_4 , are mixed in the cold. On heating, the jelly changes to a white shining crystalline powder of the same composition. The tetrahydrate loses water and forms the anhydrous salt if heated in a sealed tube with a concentrated solution of zinc chloride.

Tests for Zinc Salts.

1. Zinc salts are usually colourless.
2. Sodium hydroxide solution with a solution of a zinc salt gives a white gelatinous precipitate of zinc hydroxide, $\text{Zn}(\text{OH})_2$. This precipitate dissolves in excess of sodium hydroxide, owing to the formation of sodium zincate, which is soluble:



3. Aqueous ammonia gives a white precipitate of zinc hydroxide, soluble in excess of the precipitating reagent with formation of a complex compound, $[\text{Zn}(\text{NH}_3)_4](\text{OH})_2$.

[Addition of ammonium chloride to the solution of the zinc salt prevents precipitation by ammonia, owing to the repression of the hydroxyl ions produced by the latter.

4. Ammonium sulphide gives a white precipitate of zinc sulphide, ZnS .
5. Potassium ferrocyanide yields a white precipitate of potassium zinc ferrocyanide, $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$.
6. An alcoholic solution of resorcinol, $\text{C}_6\text{H}_4(\text{OH})_2$, to which a little ammonia has been added, is purple. On addition of a solution of a zinc salt, the colour changes to yellow, then green, and lastly deep blue.
7. If heated with sodium carbonate on a charcoal block, zinc salts leave a residue of zinc oxide, which is yellow when hot and white when cold. If moistened with cobalt nitrate solution and again heated, the residue turns green owing to the formation of cobalt zincate, CoZnO_2 ('Rinmann's green' *).

* After Sven Rinmann, 1720-92.

CADMIUM, Cd

Atomic number: 48. *Atomic weight:* 112.41. *Specific gravity:* 8.65.
Melting-point: 321°. *Boiling-point:* 767°.

History, Occurrence, and Extraction. Cadmium oxide, or *cadmia*, CdO, was discovered by STROHMEYER in 1817, in the dust in the condensers of a zinc works. KARSTEN (1819) showed that the new element was present in the zinc ores of Silesia, and the metal itself was shortly afterwards prepared by Strohmeyer by reduction of the oxide with charcoal.

Cadmium is almost entirely obtained from zinc ores (*greenockite*, CdS, the only valuable cadmium ore, is rarely found). During the distillation of the roasted zinc ores with anthracite (p. 353), the cadmium, having a lower boiling-point (767°) than zinc (907°), distils over first and is collected separately; much of it oxidizes to cadmium oxide, however, which collects as a brown powder in the condenser. The oxide is removed and re-heated with powdered anthracite. The crude cadmium is purified by electrolysis or by distillation in a vacuum.

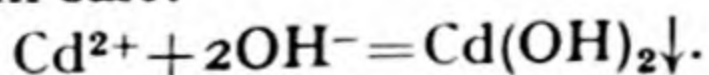
Properties. Cadmium is a fairly soft white metal, stable in dry air but becoming coated with a layer of oxide and carbonate when exposed for some time to a damp atmosphere. It dissolves in dilute acids to form salts, and is less electropositive than zinc, which therefore precipitates it from solution. In general properties, it closely resembles zinc.

Cadmium is used as a constituent of various alloys, and also for electroplating; the electrolyte consists of an aqueous solution of potassium or sodium cyanide in which cadmium cyanide has been dissolved. A coating of cadmium is much more resistant to corrosion by sea-water than one of nickel or zinc.

COMPOUNDS OF CADMIUM

Cadmium oxide, CdO, is unlike most cadmium compounds (except the sulphide) in possessing a colour. It is a brown powder made by heating the hydroxide or carbonate, or by burning the metal in air or oxygen. It dissolves in dilute acids to form salts containing the colourless bivalent ion Cd^{2+} but, in contrast to zinc oxide, it will not dissolve in aqueous alkali.

Cadmium hydroxide, $\text{Cd}(\text{OH})_2$, comes down as a white precipitate when a solution of sodium or potassium hydroxide is added to a solution of a cadmium salt:

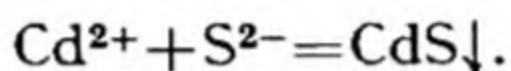


It is insoluble in excess of the alkali, but is slightly soluble in ammonia, the solution containing the complex ions $\text{Cd}(\text{NH}_3)_6^{2+}$.

Cadmium carbonate, CdCO_3 , is precipitated as a white powder when sodium *bicarbonate* is added to a solution of a cadmium salt. Sodium *carbonate* precipitates a *basic* cadmium carbonate. Both the basic and the normal carbonates dissolve in dilute acids, and yield the oxide on heating.

Cadmium chloride, CdCl_2 , is obtained as the 5:2 hydrate, $2\text{CdCl}_2 \cdot 5\text{H}_2\text{O}$, by evaporating solutions of cadmium oxide or carbonate in dilute hydrochloric acid. The anhydrous salt is best prepared by heating the metal in chlorine or hydrogen chloride (though the pentahydrate may be successfully dehydrated if heated in a current of hydrogen chloride). *Cadmium iodide*, CdI_2 , is noteworthy for its power of forming the complex anion CdI_4^{2-} (cf. HgI_4^{2-} , p. 368).

Cadmium sulphide, CdS , is well known as the pigment *cadmium yellow*. It can be made synthetically, but is usually prepared by passing hydrogen sulphide into a solution of a cadmium salt, when it is precipitated:



The solubility product of cadmium sulphide is $[\text{Cd}^{2+}][\text{S}^{2-}] = 10^{-29}$, so that when this reaction is carried out in qualitative analysis, the solution should not be too acid. The solubility product of zinc sulphide is $[\text{Zn}^{2+}][\text{S}^{2-}] = 10^{-20}$, and this substance is therefore not precipitated in acid solution (see p. 236).

For the separation of cadmium from copper in analysis see p. 318.

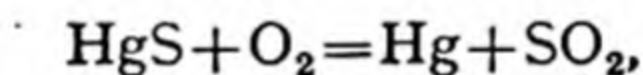
MERCURY, Hg

Atomic number: 80. *Atomic weight:* 200.61. *Specific gravity:* 13.59.
Melting-point: -39° . *Boiling-point:* 357° .

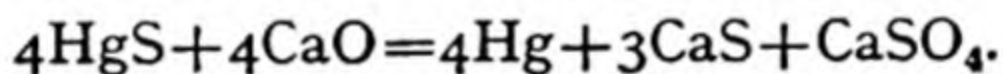
History. Mercury occurs native and has therefore been known since very early times. Among the alchemists, mercury was frequently regarded as the seed of all metals, while an alternative theory, which regarded metals as compounds of mercury with sulphur, was commonly accepted for a period of over one thousand years. The fact that mercury is definitely a metal was confirmed in 1759-60 by BRAUN, who observed that it could be solidified in a freezing-mixture.

Occurrence. Mercury is by no means abundant or widely distributed. Native, or in the form of amalgams with gold and silver (or both), it occurs in small quantity in many different localities; but the chief source of mercury is the red sulphide ore *cinnabar*, HgS. This is mined chiefly in Almaden * (Spain) and Idria (Italy), though smaller amounts are obtained from North, South, and Central America and from Russia.

Extraction. Mercury is extracted by roasting the cinnabar either (i) in air:

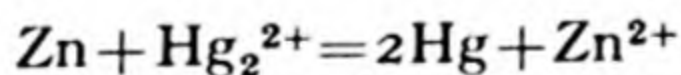


or (ii) with lime in the absence of air (i.e. in closed retorts):



In both processes the mercury distils off and the vapour is condensed in stoneware receivers.

To purify mercury it is first squeezed through chamois leather, which removes suspended impurities. It is then allowed to fall, in a series of small drops, down a glass column filled with mercurous nitrate solution or dilute nitric acid. In this way, metals more electropositive than mercury are removed by passing into solution, e.g.:



[Hg_2^{2+} is the ion of mercury in the mercurous condition.]

Metals less electropositive than mercury are afterwards removed by distillation in a vacuum, or in carbon dioxide under reduced pressure.

Properties. Mercury is a heavy liquid metal with a silvery lustre; it solidifies on cooling (M.P., -39°), boils at 357° , and has a specific gravity of 13.59.

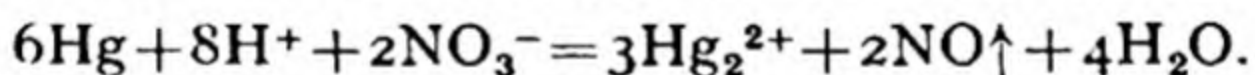
* This name is Arabic and means 'the mine': it shows that the mines were worked centuries ago during the Moorish occupation of Spain.

Mercury is appreciably volatile even at room temperature, and since the vapour—like the liquid—has pronounced toxic properties, cases of poisoning by it are by no means rare.* The classical example occurred in 1810, when H.M. ship of the line *Triumph*, of seventy-four guns, salvaged 130 tons of mercury from a Spanish wreck off Cadiz. The parchment bags in which the mercury was confined (within barrels) quickly rotted, owing to their sodden condition and to the heat of the weather, and the mercury was speedily diffused through the ship. Practically every person on board soon showed signs of mercurial poisoning, such as excessive salivation, partial paralysis, and loss of teeth; several men died, and the ship's live-stock, consisting of sheep, pigs, goats, and poultry, shared the same fate—as did also 'a canary bird . . . though the food of the latter was kept in a bottle closely corked up.' The surgeon stated that 'he had seen mice come into the ward-room, leap up to some height, and fall dead on the deck.' Only the midshipmen enjoyed a partial escape, possibly because 'these Gentlemen were almost constantly on deck' or 'out of the ship.'

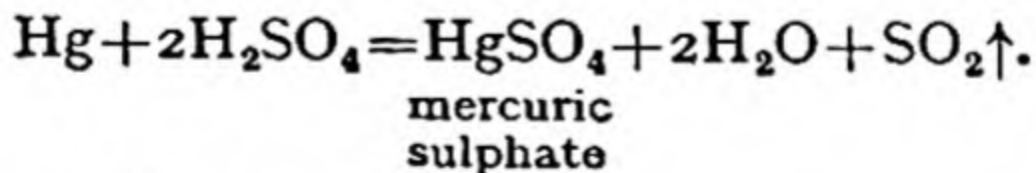
Mercury is, however, still occasionally prescribed in medicine. The celebrated (perhaps notorious) 'blue pill' consists of 1 part of metallic mercury with 2 parts of confection of roses and liquorice root.

Mercury is not attacked by air at ordinary temperatures (though ozone causes it to 'tail' or stick to glass, probably by coating it with a film of an oxide). On heating in air or oxygen, it is gradually converted into mercuric oxide, HgO ; it is, however, unaffected by water, even in the form of steam. With halogens it reacts vigorously.

Dilute hydrochloric and sulphuric acids are without action on mercury, but dilute nitric acid dissolves it to form mercurous nitrate:



Concentrated nitric acid also dissolves mercury, but in this case the mercuric salt is obtained. Concentrated sulphuric acid dissolves mercury readily on heating, with evolution of *pure* (cf. copper, p. 525) sulphur dioxide:



Alkalis have no action on mercury.

One of the most characteristic properties of mercury is its power of dissolving metals to form (a) solid or liquid solutions, or (b) definite compounds, or (c) solutions of such compounds. All these products are known by the inclusive name of *amalgams*. When

* Owing to the danger of mercurial poisoning, care should be taken not to spill mercury in the laboratory.

sodium, for example, is pressed under the surface of slightly warm mercury, it dissolves energetically, light and heat being emitted. From the amalgam so prepared it has been possible to isolate definite compounds, e.g. NaHg and NaHg_2 . Other methods of forming amalgams are:

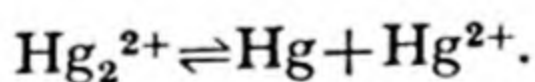
- (i) rubbing the metal with mercury (*examples*: Cu, Ag, Au);
- (ii) treating a solution of a salt of the metal with sodium amalgam (*examples*: Cu, Ag, Au, Fe, Ba);
- (iii) treating a solution of mercuric chloride with the metal (*example*: Al);
- (iv) electrolysing a solution of a salt of the metal, using a mercury cathode (*examples*: Na, Ba, Sr).

Sodium amalgam (usually written Na/Hg) is a convenient reducing agent. *Tin* amalgam (Sn/Hg) is used as the reflecting surface in cheap mirrors, and since, when freshly made, it is plastic, but soon sets hard on standing, it is used as a dental filling. *Copper* and *silver* amalgams (Cu/Hg and Ag/Hg) are also employed in dentistry. *Aluminium* amalgam (Al/Hg) is the reducing agent familiar in organic chemistry as the 'aluminium-mercury couple.' '*Ammonium* amalgam' is the peculiarly repulsive mass obtained when a concentrated solution of ammonium chloride is poured upon sodium amalgam; it rapidly decomposes, yielding ammonia, hydrogen, and mercury.

Mercury forms two series of compounds, the *mercurous*, in which it is (apparently) univalent, and the *mercuric*, in which it is bivalent.

MERCUROUS COMPOUNDS

The Mercurous Ion. The mercurous ion is not Hg^+ , but a complex ion consisting of a mercuric ion, Hg^{2+} , combined with a mercury atom, Hg. It is represented as Hg_2^{2+} or $\text{Hg}^+ - \text{Hg}^+$, and is unique in the chemistry of the metals: mercury is therefore bivalent in both of its series of compounds. In solution, the mercurous ion shows some—though little—tendency to dissociate into its constituents:



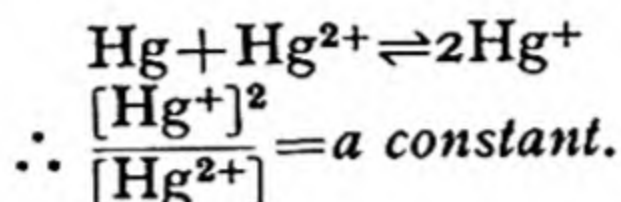
If mercury is shaken with mercuric nitrate solution some of it is dissolved and mercurous nitrate is formed. An investigation of the mechanism of this last reaction confirms the double formula Hg_2^{2+} for the mercurous ion, since it has been found that, at equilibrium, the ratio $\frac{[\text{mercurous ion}]}{[\text{mercuric ion}]}$ in the solution is constant.

This is what would be expected from the equation $\text{Hg} + \text{Hg}^{2+} \rightleftharpoons \text{Hg}_2^{2+}$

if excess of metallic mercury is present. Representing concentrations in the usual way, we see that $\frac{[\text{Hg}_2^{2+}]}{[\text{Hg}]} = \text{a constant}$. But $[\text{Hg}]$ is also constant (since excess is present),

$$\therefore \frac{[\text{Hg}_2^{2+}]}{[\text{Hg}]} = K.$$

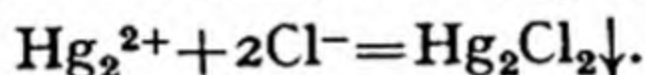
Had the mercurous ion been Hg^+ , the expression would have become:



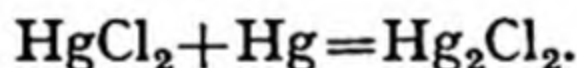
That is, the concentration of the mercuric salt at equilibrium would have been proportional to the *square* of the concentration of the mercurous salt.

Mercurous oxide. The black, or nearly black, powder precipitated when a solution of an alkali hydroxide is added to a solution of a mercurous salt (e.g. the nitrate) was at one time thought to be mercurous oxide. X-ray analysis, however, shows it to be a mixture of mercuric oxide, HgO , with metallic mercury.

Mercurous chloride, or calomel, Hg_2Cl_2 . This compound is insoluble in water and may therefore be obtained by adding a soluble chloride to a solution of a mercurous salt, e.g. the nitrate:

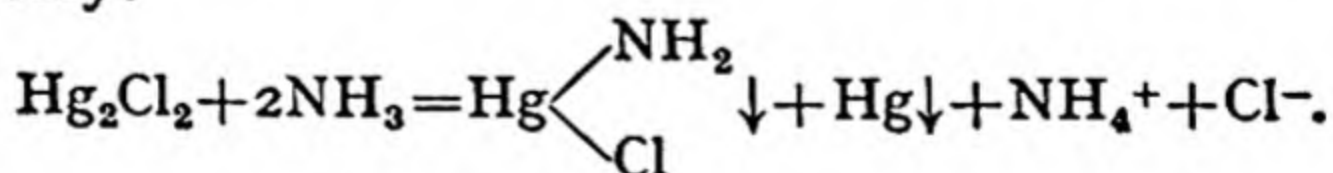


It may also be prepared by heating a mixture of mercuric chloride with mercury:



The mercurous chloride sublimes on to the cooler parts of the apparatus; it is washed with water, to remove any remaining mercuric chloride—which is poisonous—and with dilute nitric acid to remove mercury.

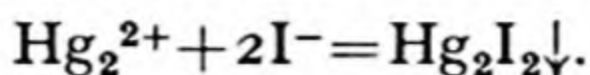
On addition of aqueous ammonia, mercurous chloride is turned black (hence, perhaps, the name *calomel*, 'fine black'). The black substance is believed to be a mixture of amino-mercuric chloride and mercury:



Calomel is used in medicine as a purgative (dose 0.03–0.30 gm.) and in ointments (e.g. *unguentum hydrargyri subchloridi*).

On vaporization calomel dissociates into mercury and mercuric chloride and the V.D. is half that calculated.

Mercurous iodide, Hg_2I_2 , is obtained as a yellow precipitate when potassium iodide solution is added to mercurous nitrate solution:

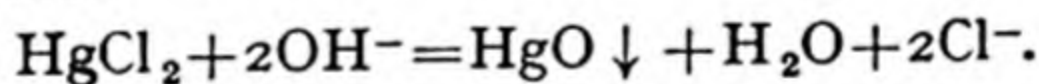


It is unstable and soon turns green, possibly owing to the liberation of mercury. A similar green substance is produced by triturating mercury and iodine together in the proportions demanded by the formula Hg_2I_2 .

Mercurous nitrate, $\text{Hg}_2(\text{NO}_3)_2$, is a colourless crystalline solid prepared by dissolving mercury in cold dilute (1 : 2½) nitric acid and allowing the solution to stand. It is exceptional among mercury compounds in forming a hydrate, $\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, the crystals of which effloresce on exposure to air. Like the corresponding mercuric salt, mercurous nitrate in solution may be precipitated as a whitish basic salt; this will, however, re-dissolve on addition of a slight excess of nitric acid.

MERCURIC COMPOUNDS

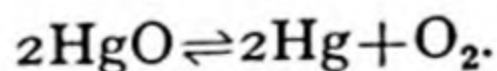
Mercuric oxide, HgO , is well known for the decisive part it played in the downfall of the phlogiston theory at the hands of LAVOISIER. It is formed as a red crystalline solid when mercury is heated in air or oxygen at a temperature slightly below its boiling-point; but this method is very tedious. A better way is to precipitate the oxide by addition to hot aqueous caustic alkali of a solution of mercuric chloride:



We might here have expected to get mercuric hydroxide, but this compound, like its mercurous counterpart, is unknown.

When prepared by precipitation, mercuric oxide is yellow or orange, but the difference between the red and yellow forms is probably due to nothing more than a difference in fineness of the particles.

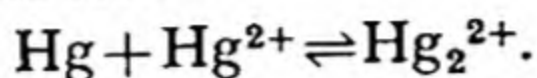
Mercuric oxide decomposes into mercury and oxygen on heating to 500° – 600° :



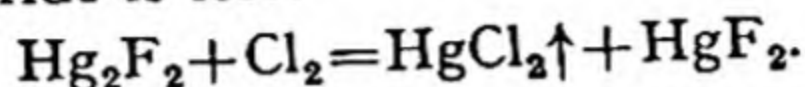
It is a basic oxide, and dissolves in acids to form solutions of mercuric salts.

The Mercuric Ion. The mercuric ion is Hg^{2+} , but it is a remarkable fact that many mercuric salts show very little readiness to form it. Thus, while mercuric nitrate and fluoride are highly ionized, the other mercuric halides and mercuric cyanide are covalent compounds. On the other hand, the mercuric ion forms complex cations (e.g. $[\text{Hg} \cdot 2\text{NH}_3]^{2+}$) and anions (e.g. $[\text{HgI}_3]^-$). If agitated

with mercury, mercuric ions in aqueous solution are almost wholly converted into mercurous ions:

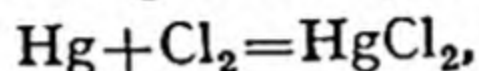


Mercuric fluoride, HgF_2 , is prepared anhydrous by heating mercurous fluoride in a stream of chlorine; mercuric chloride sublimes away and the fluoride is left:

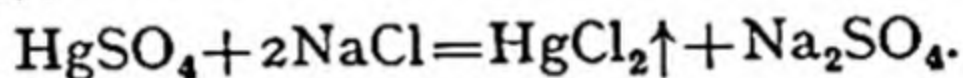


It is a colourless crystalline solid, M.P. 645° . In solution it is distinguished from the other mercuric halides by being strongly ionized. If the solution is evaporated, hydrogen fluoride is evolved and a residue of mercuric oxide remains.

Mercuric chloride, HgCl_2 , is commonly known as *corrosive sublimate*. It may be obtained by heating mercury in an excess of chlorine:



or—as in chemical industry—by a method suggested as long ago as 1716 by KUNCKEL. This consists in heating a mixture of equal parts of dry sodium chloride and mercuric sulphate, with the addition of a little manganese dioxide to oxidize any mercurous chloride formed from the mercurous sulphate almost always present in commercial mercuric sulphate:

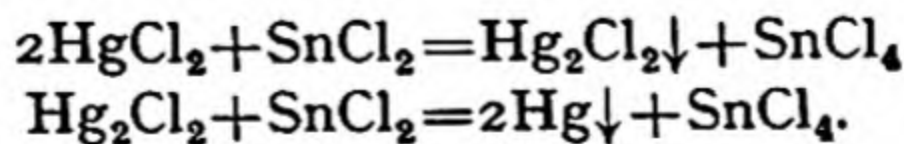


The mixture is heated in large, long-necked glass flasks, into the upper portions of which the mercuric chloride sublimes. On cooling, the flasks are broken and the lumps of sublimate removed.

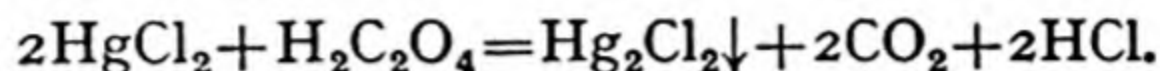
Mercuric chloride crystallizes in colourless rhombic needles, soluble in water, methyl alcohol, ethyl alcohol, ether, and acetone. Figures given for the solubility in water differ in different authorities; roughly, the solubility is 5 at 10° and 60 at 100° . The salt may be largely extracted from aqueous solution by shaking with ether; it melts at about 270° and boils at about 300° .

An aqueous solution of mercuric chloride will turn blue litmus red but does not affect methyl orange. The degree of dissociation of mercuric chloride in the ordinary bench solution is so small as to be negligible.

Mercuric chloride is easily reduced to mercurous chloride or even to metallic mercury. Thus when stannous chloride is added to mercuric chloride solution a white precipitate of mercurous chloride is formed at first, but this ultimately turns grey owing to the liberation of finely divided mercury:



The rate of reduction of mercuric chloride by oxalic acid in the presence of light is a measure of the intensity of the illumination (Eder's *chemical photometer*):



A trace of iron must be present to catalyse the action.

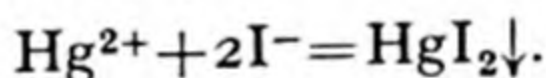
When ammonia is added to mercuric chloride in aqueous solution it gives a white precipitate ('infusible white precipitate') of amino-

mercuric chloride (see p. 365), $\text{Hg} \begin{matrix} \text{NH}_2 \\ \text{Cl} \end{matrix}$. If, however, gaseous

ammonia is passed into a solution of mercuric chloride in acetone, a white addition product is obtained; this is known as 'fusible white precipitate' and has the formula $[\text{Hg}(\text{NH}_3)_2]\text{Cl}_2$.

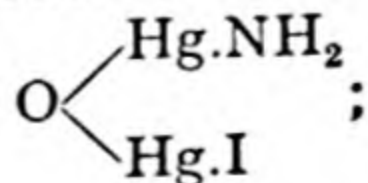
Mercuric chloride is intensely poisonous, particularly to the lower forms of life; hence, in dilute solution, it is used as an antiseptic, disinfectant, and preservative. To human beings it may prove fatal in doses as small as 0.19 gm. The best antidote is raw white of egg with plenty of water.

Mercuric iodide, HgI_2 , may be obtained synthetically by rubbing iodine and mercury together in the proportions demanded by the formula, but is usually prepared by adding a solution of an iodide to a solution of a mercuric salt:

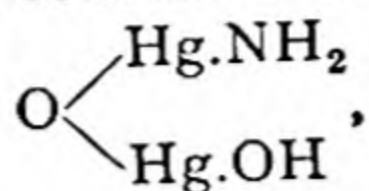


It is precipitated as a yellow solid which almost instantaneously turns scarlet. Of these two different forms of mercuric iodide the red is stable up to $127-8^\circ$, but above this temperature (the transition temperature) the yellow modification is the stable one. If the red form is heated it turns yellow above 127° ; on cooling, the yellow form persists for some time, but changes to red on standing or on rubbing with a cork or a glass rod.

Mercuric iodide dissolves in excess of potassium iodide solution, forming the complex mercuri-iodides KHgI_3 and K_2HgI_4 , with the respective anions HgI_3^- and HgI_4^{2-} . The concentration of mercuric ion, Hg^{2+} , in solutions of these compounds is so small that no precipitate of mercuric oxide is obtained on addition of alkali. An alkaline solution of potassium mercuri-iodide will, however, give a yellowish-brown precipitate with ammonia, and is used under the name of *Nessler's solution* as a delicate test for ammonia and ammonium salts. The structure of the precipitate is probably

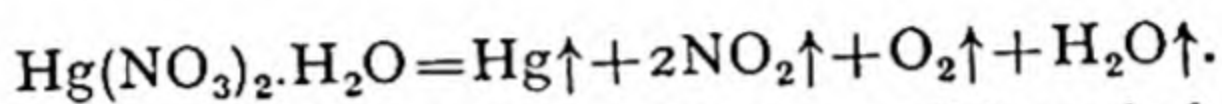


on this view it is the iodide of MILLON's base,

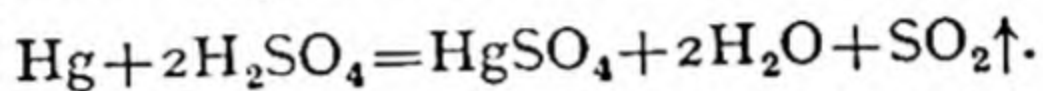


a yellow solid made by the action of a warm aqueous solution of ammonia upon mercuric oxide.

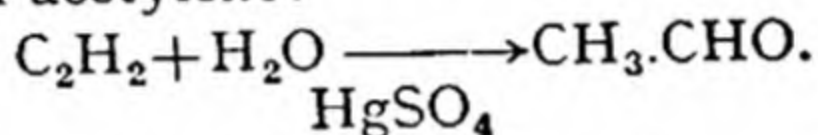
Mercuric nitrate, $\text{Hg}(\text{NO}_3)_2$, is made by dissolving mercury in an excess of hot concentrated nitric acid and allowing the solution to crystallize. Colourless deliquescent crystals of the monohydrate, $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, or hemihydrate, $2\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, are obtained. From solution, unless nitric acid is added, basic nitrates are liable to be precipitated. On heating, mercuric nitrate decomposes into products which are all either gaseous or volatile, so that no residue is left:



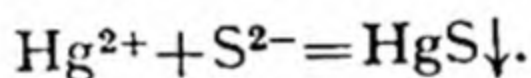
Mercuric sulphate, HgSO_4 , is a colourless solid made by the action of hot concentrated sulphuric acid on mercury; the acid must be in excess:



It is important as the catalyst in the industrial preparation of acetaldehyde from acetylene:



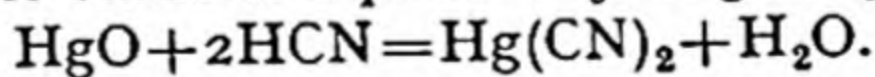
Mercuric sulphide, HgS , is precipitated as a black powder when hydrogen sulphide is passed into a solution containing mercuric ions, and is one of the most insoluble substances known (solubility product, 10^{-52}):



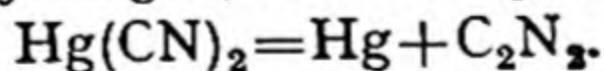
It may also be obtained synthetically.

The black form changes to bright red when heated with aqueous alkalis, the red form finding application in the arts as the pigment *vermilion*. Native mercuric sulphide is *cinnabar*.

Mercuric cyanide, $\text{Hg}(\text{CN})_2$, is a covalent substance made by dissolving mercuric oxide in aqueous hydrogen cyanide:



It is used to prepare cyanogen, which it yields on heating:



Tests for Mercury.

1. Mix with dry sodium carbonate in excess and heat in hard-glass tube. A metallic mirror of mercury is often obtained.

2. *Mercuric salts.*

- (a) Potassium or sodium hydroxide: yellow precipitate of mercuric oxide.
- (b) Ammonia solution: white precipitate of amino-mercuric chloride (infusible white precipitate). See p. 368.
- (c) Hydrogen sulphide: black precipitate of mercuric sulphide, HgS .
- (d) Potassium iodide: yellow precipitate (immediately turning red) of mercuric iodide, HgI_2 ; soluble in excess.
- (e) A solution of cobalt nitrate and potassium thiocyanate: deep blue precipitate of cobalt mercuric thiocyanate, $\text{Co}[\text{Hg}(\text{SCN})_4]$.

3. *Mercurous salts.*

- (a) Dilute hydrochloric acid: white precipitate of calomel, Hg_2Cl_2 , blackened by ammonia.
- (b) Potassium chromate: brick-red precipitate of mercurous chromate, Hg_2CrO_4 .
- (c) Potassium iodide: greenish-yellow precipitate of mercurous iodide, Hg_2I_2 .

COMPARATIVE EXERCISES

- 1. Compare the properties of cadmium with those of (a) mercury and (b) zinc. To which element is it the more similar?
- 2. Tabulate the principal resemblances and differences between zinc and mercury and between zinc compounds and mercury compounds.
- 3. Make a similar table for mercury and silver.

CHAPTER XXVI

GROUP III

BORON, ALUMINIUM

Boron—Aluminium $\left\{ \begin{array}{l} \text{Scandium—Yttrium—Lanthanum, etc.} \\ \text{Gallium—Indium—Thallium} \end{array} \right.$

BORON, B

Atomic number : 5. Atomic weight : 10.82. Density : 2.310. Melting-point : 2,300° (?). Boiling-point ?

History. The word *borax* is derived from the Arabic *buraq* ('white and shining'), a term applied to Mohammed's winged steed and to many substances used by the Arab chemists as fluxes. One such substance, *tincal*, obtained from Tibet, India, and Armenia, is the compound $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, sodium pyroborate, or simply 'borax.' In the Middle Ages, borax was imported into Europe from Central Asia, Venice being the centre of purification of the crude tincal. In 1702, HOMBERG prepared boric acid (*sal sedativum*) by heating borax with ferrous sulphate, and in 1747–8 BARON discovered that borax is a compound of *sal sedativum* and soda; he suggested therefore that the so-called *sal* was not a salt but an acid. LAVOISIER regarded boric acid as the oxide of an element, and in 1807 DAVY obtained an impure specimen of this element by electrolysis of fused boric acid anhydride (boron trioxide, B_2O_3).

In 1808, GAY-LUSSAC and THENARD prepared a purer specimen by heating boron trioxide with potassium in a copper tube, a method also employed by Davy in the same year. The Frenchmen called the new element *bore*, while Davy, under the impression that it was metallic, gave it the name *boracium*. Four years later, however, he realized that it was non-metallic, and altered 'boracium' to *boron*, by analogy with 'carbon.'

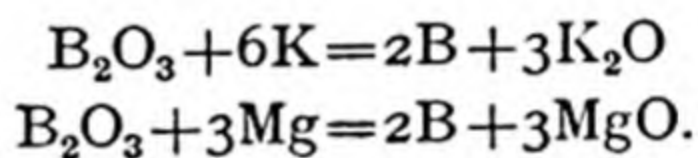
Occurrence. Free boron does not occur in nature, and although it is fairly widely distributed in the form of its compounds, workable deposits of boron minerals are relatively few. Natural boron compounds consist almost invariably of borates or boro-silicates, the former being the more important. The principal deposits occur in the Mojave Desert of California, where vast quantities of *kernite*, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$, *colemanite*, $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$, and *ulexite*,

$\text{NaBO}_2 \cdot \text{CaB}_4\text{O}_7 \cdot 8\text{H}_2\text{O}$ are found in the Kern County and Searles Lake districts. Other large borate deposits occur in Bolivia, Chile, Peru, and Anatolia (Turkey). The deposits of borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, in Tibet, are still worked on a small scale.

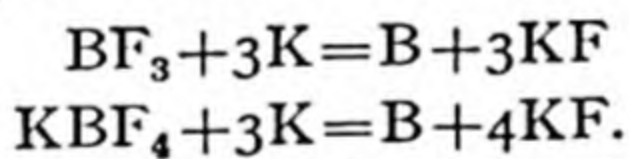
In the province of Pisa (Italy)—a volcanic region—jets of steam called *soffioni* issue from cracks in the rocks. The steam carries with it not only some 3 per cent by volume of carbon dioxide, nitrogen, hydrogen, helium, hydrogen sulphide, etc., but about 0.06 per cent by weight of boric acid. The boric acid is extracted in the way described below (p. 374). In many other volcanic districts, e.g. Chile, Tibet, and Kashmir, hot springs containing boric acid are widespread.

In living organisms, boron occurs normally in only the minutest proportion, e.g. one part in 100,000,000; traces of it are, however, necessary to plant growth. Except in very small quantities, boron compounds are poisonous to all forms of life.

Preparation. Boron can be obtained by strongly heating boric oxide (boron trioxide), B_2O_3 , with sodium, potassium, or, preferably, magnesium:



It is also formed when boron fluoride, BF_3 , or potassium fluoborate, KBF_4 , is heated with potassium:



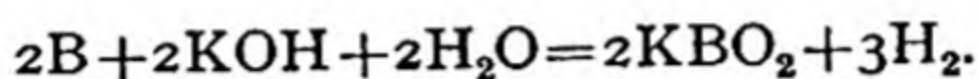
When boron trioxide is strongly heated with aluminium in a graphite crucible, a dark-coloured, very hard crystalline substance is produced which was formerly taken to be elementary boron. X-ray analysis has however shown that it is a definite compound of composition $\text{B}_{44}\text{C}_2\text{Al}_3$. The pure element has recently been obtained by exposing a mixture of vaporized boron tribromide (B.P. 91°) and hydrogen to a tantalum filament heated electrically to $1,300^\circ$, when black crystals develop along the filament. In this form boron is chemically very inactive, and, unlike aluminium, an insulator.

Properties. As prepared by the reduction of boron compounds with potassium or magnesium, boron is a brown, dark green, or even maroon, amorphous powder. This is stable in air at ordinary temperatures, but on heating to 700° burns with a brilliant green flame; the combustion quickly ceases, however, owing to the formation of a protective layer consisting of boron trioxide mixed with a little boron nitride, BN.

Amorphous boron can be fused at a high temperature, and the fused mass on cooling hardens to an opaque black solid; this shows

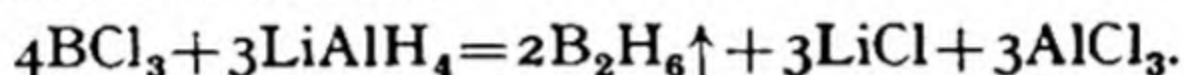
a curved or conchoidal fracture and is therefore presumably non-crystalline. It differs from boron in powder form inasmuch as it may be strongly heated in air without undergoing oxidation.

Amorphous boron does not dissolve in water, but energetically reacts with steam at a red heat, forming boric acid and hydrogen; at similar temperatures it will also reduce the oxides of carbon to carbon. It combines with all the halogens, fluorine attacking it even in the cold. If heated together, amorphous boron and sulphur combine with incandescence to form *boron sulphide*, B_2S_3 , which is a white crystalline solid. If fused with alkalis, boron yields borates and hydrogen:

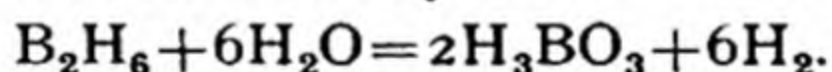


COMPOUNDS OF BORON

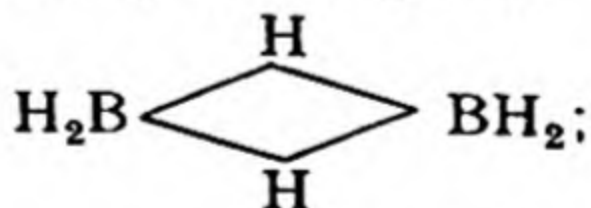
Boron hydrides. Two ethereal solutions, one of the powerful reducing agent lithium aluminium hydride (p. 280), and the other of boron trichloride (B.P. 12°), are strongly cooled, mixed, and then allowed to regain normal temperature, when *diborane* is liberated in almost quantitative amount:



Diborane, B_2H_6 , is a colourless gas (B.P. -92°) with characteristic odour. It is inflammable, though in air not spontaneously, and reacts with water almost instantly:



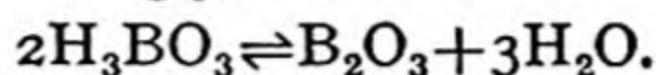
When a mixture of carbon monoxide and diborane is heated under pressure at 100° , *borine carbonyl*, $H_3B.CO$, is formed. In this compound the link $B-C$ is similar to that between B and N in $F_3B.NH_3$ (p. 109). Unlike its methyl derivative, $B(CH_3)_3$, free borine, BH_3 , has apparently no stable existence. The constitution of diborane is represented by the diagram:



the terminal hydrogen atoms are linked to boron by ordinary localized electron pair bonds, while the two central bonds each contain a 'delocalized' electron pair which binds all the three atoms B, H, B (cf. ozone, p. 120).

Higher boranes, such as *tetraborane*, B_4H_{10} (B.P. 18°), *pentaborane*, B_5H_9 (B.P. 48°), *decaborane*, $B_{10}H_{14}$ (M.P. 100°), are produced by circulating diborane through heated tubes under controlled conditions of pressure and temperature.

Boron trioxide, B_2O_3 , is left as a colourless, glass-like residue when boric acid, H_3BO_3 , is strongly heated:



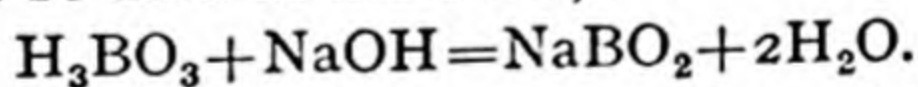
It is the anhydride of boric acid, which it very slowly re-forms when added to water.

When an aqueous solution containing both boric and phosphoric acids is evaporated to dryness and the product gently heated, a colourless, crystalline product results, of composition BPO_4 . This was formerly called 'boron phosphate' and was considered to indicate an amphoteric character for boron. Chemically, however, it behaves as a mixed anhydride of boric and phosphoric acids, and analysis by X-ray methods confirms this constitution: it should therefore be termed *boro-phosphoric anhydride*.

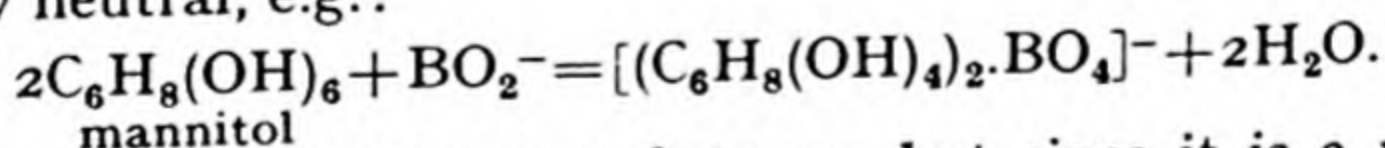
Boric acid, H_3BO_3 , is obtained from the *soffioni* (p. 372) by condensing the steam and concentrating the liquid in lead pans, the necessary heat being derived from the *soffioni* themselves. On cooling the concentrated solution, boric acid crystallizes out.

The bulk of the boric acid output is, however, made by adding an excess of sulphuric acid to a boiling saturated solution of borax. When the mixed solutions are cooled, boric acid separates out. It can be purified by recrystallization from water.

Boric acid—properly *orthoboric acid*, and popularly 'boracic acid'—is a colourless crystalline solid with a greasy feel; it dissolves slightly in cold water and readily in hot water. It is a very weak acid, and borate anions are therefore strong bases. Boric acid can, however, be titrated (as a *monobasic acid*) with sodium hydroxide if an excess of glycerol, mannitol, or dextrose is added to the solution, the point of equivalence being reached at $pH \approx 8-9$ (hence phenolphthalein should be used as indicator):

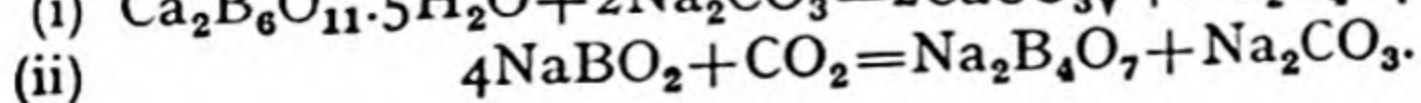
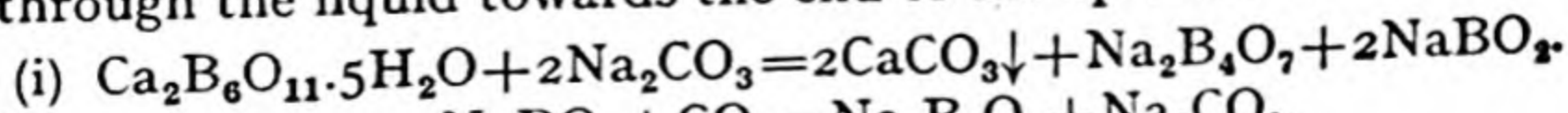


The neutralization effectively stops at the point shown in this equation, because the metaborate anion BO_2^- condenses with the added organic hydroxy-compound to form a complex anion which is nearly neutral, e.g.:



Boric acid is a poisonous substance, but since it is a powerful germicide it was at one time used as a food preservative.

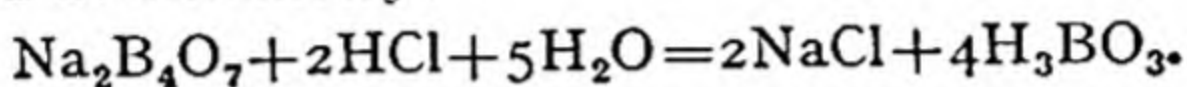
Sodium tetraborate, borax, $Na_2B_4O_7 \cdot 10H_2O$, is made from colemanite and ulexite (p. 371) by boiling the finely ground ore with sodium carbonate solution, a current of carbon dioxide being forced through the liquid towards the end of the operation:



The precipitate of calcium carbonate is filtered off and the filtrate allowed to cool, when the borax crystallizes out. It is purified by recrystallization.

On heating, borax loses water and froths up into a voluminous white mass, which at a higher temperature melts to a colourless glass of the anhydrous salt. The presence of compounds of certain metals in the fused borax may cause the 'glass' to assume a definite colour, owing to the formation of coloured metaborates, and this is the basis of the 'borax bead' test.

Borax is alkaline in solution, since $B_4O_7^{2-}$ is a strong anion-base. It can be titrated against hydrochloric acid, methyl orange or bromphenol blue being used as indicator, and has been recommended as a standard in acidimetry:



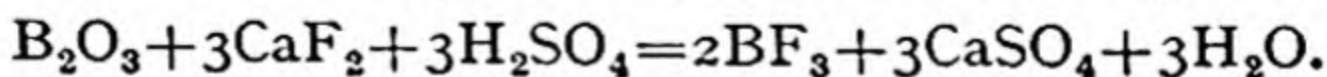
Borax is largely employed in glass manufacture, since boron glasses (e.g. Pyrex) possess a low coefficient of expansion and useful optical properties. It is also used by laundrymen to soften hard water, and to give a gloss to linen when ironed.

Sodium perborate. A compound known by this name is obtained by the electrolysis of, or by adding sodium peroxide or hydrogen peroxide to, a cooled solution of borax and sodium hydroxide. It is a colourless crystalline compound corresponding to the formula $NaBO_3 \cdot 4H_2O$. In solution, however, it behaves like a compound of sodium metaborate and hydrogen peroxide, and the solid substance is perhaps best regarded as sodium metaborate with 3 molecules of water of crystallization and one molecule of hydrogen peroxide of crystallization, i.e. $NaBO_2 \cdot H_2O_2 \cdot 3H_2O$.

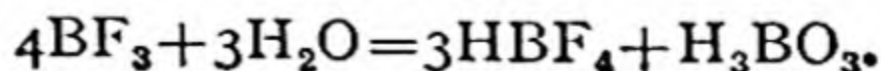
On heating, sodium 'perborate' melts and decomposes, yielding sodium metaborate, water, and oxygen. Its aqueous solution which has oxidizing and germicidal properties, gradually decomposes in the cold, forming caustic soda, hydrogen peroxide, and borax; the decomposition is greatly accelerated by heating, and oxygen is evolved.

Sodium 'perborate' is used as a cleansing and bleaching agent, e.g. in tooth-pastes and soaps and in the dye industry. It is also employed in electroplating solutions, since it prevents 'hydrogen pitting' and thus gives a smoother and better deposit.

Boron trifluoride, BF_3 , is a colourless, fuming gas made by heating boron trioxide and fluorspar with concentrated sulphuric acid:

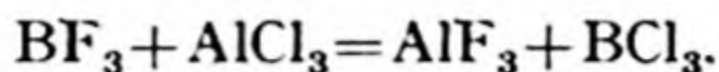


It is dissolved and decomposed by water, the solution containing boric acid and *fluoboric acid*, HBF_4 :

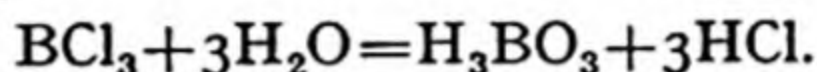


Neither aqueous fluoboric acid nor solutions of its salts attack glass. Potassium fluoborate is only slightly soluble in water and is precipitated from a solution of fluoboric acid on addition of potassium hydroxide.

Boron trichloride, BCl_3 , is best made by passing a current of boron trifluoride over gently heated aluminium chloride:



It is a colourless vapour, easily condensed in a freezing-mixture to a liquid boiling at 12° – 13° . Water hydrolyses it to boric and hydrochloric acids:

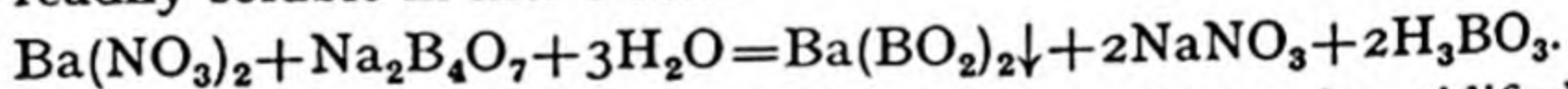


In this respect it resembles phosphorus trichloride (p. 466).

Tests for Borates.

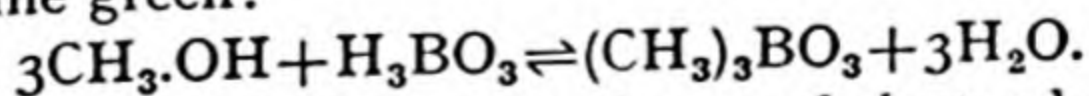
1. With a cold, concentrated solution of a borate neutralized by the addition of nitric acid, silver nitrate gives a white precipitate, soluble in excess of nitric acid. This precipitate, which consists of silver metaborate, AgBO_2 , darkens on heating, owing to the formation of silver oxide.

2. With a neutral solution of a borate, barium nitrate solution gives a white precipitate of barium metaborate, $\text{Ba}(\text{BO}_2)_2$, readily soluble in nitric acid:



3. If a piece of turmeric paper is dipped into a strongly acidified solution of a borate, it remains yellow but turns brown on drying. On addition of sodium hydroxide solution, the colour changes from brown to bluish-black. (Notice that the usual reaction of turmeric is *yellow* in acid solution, *brown* in alkaline solutions; its behaviour in the above test remains unexplained.)

4. If a solid borate is mixed with methyl alcohol and concentrated sulphuric acid and the alcohol then ignited, a green-edged flame results. This is due to the formation of the volatile compound *methyl borate*, $(\text{CH}_3)_3\text{BO}_3$, the combustion of which tinges the alcohol flame green:



Ethyl (ordinary) alcohol may be used instead of methyl alcohol, but does not give such good results.

The function of the sulphuric acid is to take up the water formed and thus prevent the reversible hydrolysis of the methyl borate.

ALUMINIUM, Al

Atomic number: 13. Atomic weight: 26.98. Specific gravity: 2.7.
Melting-point: 659°. Boiling-point: about 2,200°.

History. The Romans were familiar with alum, which they called *alumen*: hence the name 'aluminium' for the metal. PORT in 1746 showed that alum is a compound containing a metallic earth, and in 1782 LAVOISIER suggested that this earth, *alumina*, was a metallic oxide. In 1827 WÖHLER obtained metallic aluminium, by heating the anhydrous chloride with metallic potassium.



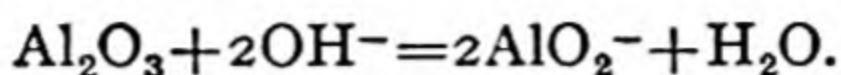
British Aluminium Co.

FIG. 69. MINING BAUXITE

Occurrence. Aluminium is the most abundant metal, and the third most abundant element, in the earth's crust. Its compounds are not merely plentiful but very widely distributed, principally in the form of *aluminosilicates* (e.g. clay, kaolin, mica, feldspar, and slate). Aluminium oxide, Al_2O_3 , occurs anhydrous as *corundum* or *emery*, *sapphire*, and *ruby*, and in the hydrated form as *bauxite*, $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, and *hydrargillite*, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. *Cryolite* (ice-stone), Na_3AlF_6 , occurs in Greenland. *Turquoise* is basic aluminium phosphate, its bluish-green colour being due to the presence of traces of copper phosphate.

Extraction. It has been reported that a commercially successful method of obtaining aluminium from clay is in use in Russia, but elsewhere the metal is extracted from bauxite, large deposits of which occur in France, Ireland, South America, and Bengal. Bauxite is invariably contaminated with silica and ferric oxide, and the first

stage in its treatment is the removal of these substances. The crude bauxite is heated with caustic soda solution under pressure, when sodium aluminate and silicate pass into solution while the ferric oxide remains unaffected:



The insoluble matter is filtered off, and the filtrate is treated with a little precipitated aluminium hydroxide; this causes precipitation of about three-quarters of the aluminium in the solution, in the form of aluminium hydroxide. The silicate, however, is not decomposed. The action of the added aluminium hydroxide is obscure; it is known that, on standing, aluminium hydroxide changes into a less

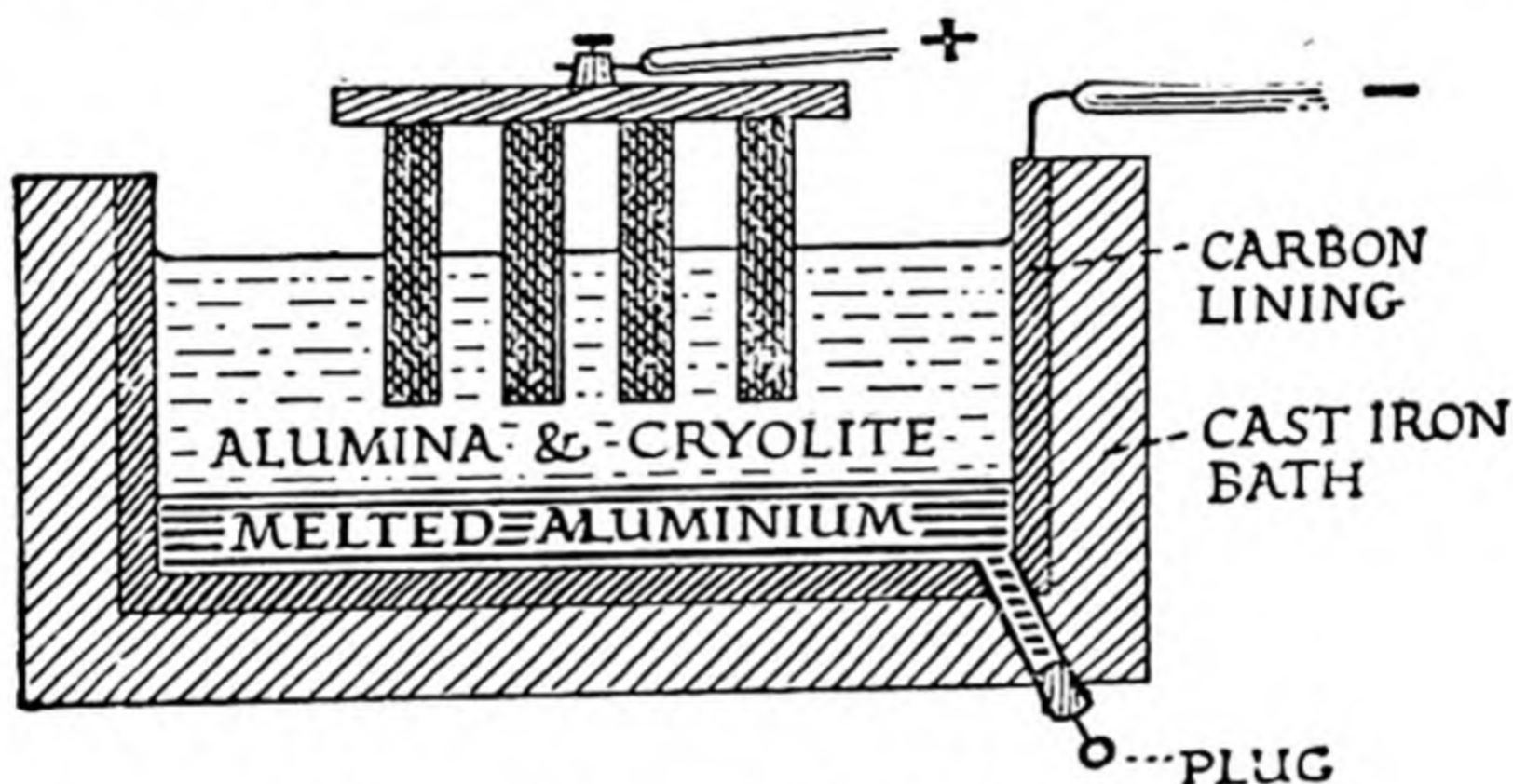
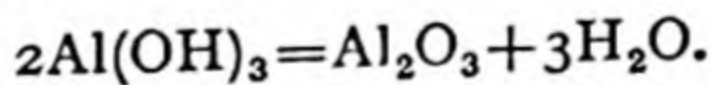


FIG. 70. MANUFACTURE OF ALUMINIUM

soluble form, and it may be that addition of a little of this more or less insoluble modification causes the hydroxide, $\text{HO}\cdot\text{AlO}$, formed in the solution from the strong anion-base AlO_2^- , to undergo a rapid change into the same modification.

The precipitated hydroxide is washed and strongly heated, yielding pure alumina:

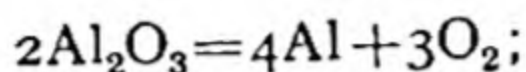


The removal of iron is rendered necessary by the fact that the extraction of aluminium is electrolytic, and since iron is less electro-positive than aluminium it would be liberated and thus contaminate the latter. Aluminium containing iron is so easily corroded as to be practically worthless.

The pure alumina is dissolved in molten cryolite (formerly obtained from Greenland but now prepared synthetically) in an iron box lined with carbon; this forms the cathode. The anodes consist of carbon

rods suspended in the molten electrolyte. On passing the current (E.M.F. 5.5 volts) molten aluminium collects on the floor of the box and oxygen is liberated at the anodes, slowly burning them away to oxides of carbon. The furnace is tapped from time to time, to run off the aluminium, and fresh alumina is added as required.

The course of the electrolysis is uncertain. The net result is:



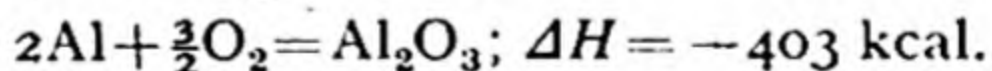
if the decomposition potentials of alumina, aluminium fluoride, and sodium fluoride estimated as respectively 2.0, 4.0, and 4.7 volts are correct, then only the oxide undergoes electrolysis.

The electrolytic process for aluminium extraction was invented independently in 1886 by HALL (America) and HÉRAULT (France).

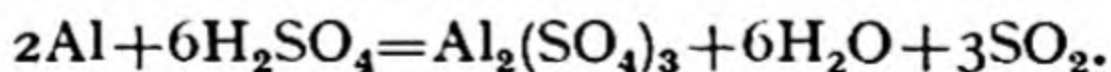
Properties. Aluminium is a white metal of low density (2.7 gm. per c.c.); it melts at 659°, and boils at a high temperature, probably about 2,500°. In spite of its high position in the electrochemical series (p. 244), it is resistant to air, and does not attack water when pure, owing in both cases to the formation of a thin coherent but invisible film of oxide. If this film is removed, the surface re-oxidizes quickly, but, owing to the strongly protective nature of the film, the latter remains of extreme thinness, and does not appreciably impair the reflecting power of the metal: large aluminium mirrors are now widely used in astronomical apparatus, wherein their low mass is a great advantage.

Pure aluminium is too soft for use in common articles: it is therefore always alloyed with about 5 per cent of copper and smaller amounts of other metals.

When strongly heated in the air, aluminium burns with great evolution of heat, forming the oxide:



It readily combines with the halogens, and reacts with hydrogen chloride to form aluminium chloride and hydrogen. It dissolves easily in hydrochloric acid, but dilute sulphuric acid scarcely attacks it, perhaps because a protective film of the basic sulphate is formed. Hot concentrated sulphuric acid dissolves aluminium, with liberation of sulphur dioxide:



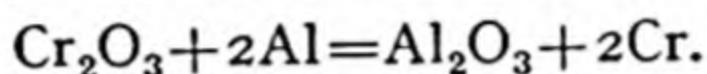
Nitric acid (concentrated or dilute) renders the metal passive (p. 246), so that aluminium containers may conveniently be used for transporting and storing this acid. Aluminium kettles 'furred' with calcium carbonate from hard water may be safely cleaned with dilute nitric acid.

Aluminium is dissolved by solutions of caustic alkalis, with formation of aluminates and evolution of hydrogen:

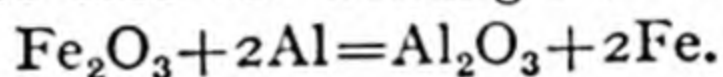


The concentration of OH^- ions in sodium carbonate solution is high enough to bring about this reaction slowly. Aluminium saucepans, etc., should therefore not be cleaned with washing-soda, neither should soda be added to any water they contain.

In the form of powder, aluminium is used as a reducing agent in the preparation of metals by the GOLDSCHMIDT process. A mixture of the metallic oxide with aluminium powder is placed in a Battersea crucible and ignited by means of a piece of burning magnesium ribbon. Reduction occurs and the desired metal is left—usually in the fused state—at the bottom of the crucible, e.g.:



A mixture of ferric oxide and aluminium powder undergoes a similar reaction, intense heat being developed. This mixture is known as 'thermit,' and can be used for welding iron objects.



COMPOUNDS OF ALUMINIUM

Aluminium forms the tripositive cation Al^{3+} , and may also form the aluminate anion, AlO_2^- .

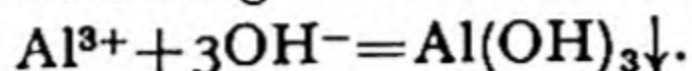
Aluminium oxide, Al_2O_3 , commonly known as alumina, is a white solid which in its impure natural form, *emery*, is used as an abrasive, e.g. in emery-paper. *Sapphire* is transparent crystalline alumina (corundum) coloured by small quantities of chromium or cobalt oxides; *ruby* is corundum coloured with chromium sesquioxide, Cr_2O_3 ; in *oriental amethyst* the colour is due to traces of manganese. Similar gems can be made artificially by dissolving appropriate metallic oxides in fused alumina.

Alumina can be prepared by burning the metal in air or in oxygen, or by heating the hydroxide or nitrate. It is formed as white feathery outgrowths if a piece of aluminium is amalgamated on the surface with mercury and then exposed to the air. Scratching the aluminium with a crystal of mercuric chloride forms sufficient amalgam for this action to take place. The presence of the mercury prevents the formation of a continuous protective film, and the true chemical activity of aluminium is thus revealed.

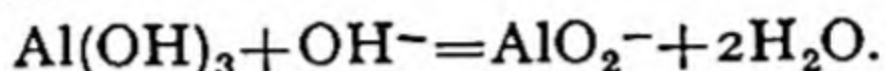
Aluminium oxide which has not been heated to a higher temperature than dull redness will dissolve in acids to form salts, and in caustic alkali solutions to form aluminates; it is therefore *amphoteric*. Strong heating converts it into a denser modification insoluble in aqueous acids and alkalis, but soluble in fused alkali.

If bauxite is roasted with lime, *bauxite cement* is formed. This is resistant to the action of sea-water and is largely used in making dock walls, sea embankments, and moles.

Aluminium hydroxide, $\text{Al}(\text{OH})_3$, is precipitated as a colourless gelatinous mass by the addition of a solution of ammonia or caustic alkali to a solution containing aluminium ions:



The precipitate is unaffected by excess of ammonia solution, but dissolves in excess of caustic alkali, owing to formation of the soluble aluminates:



Aluminium hydroxide is weakly basic and is insoluble in water. When freshly prepared, it dissolves in both acids and alkalis, but on standing it becomes converted into an insoluble modification. If heated to dull redness it yields a residue of alumina.

Aluminium hydroxide has remarkable powers of adsorbing colloidal particles and dyes. It is therefore used in precipitating the colloidal and suspended matter in sewage, and in the dye industry (see p. 384).

Aluminium carbonate does not exist. Addition of sodium carbonate solution to a solution of an aluminium salt precipitates aluminium *hydroxide*.

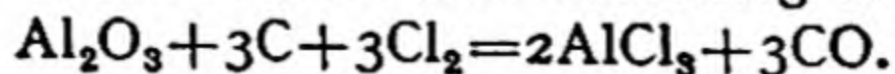
Aluminates. When aluminium hydroxide dissolves in alkali, it appears to act as an acid, forming substances called aluminates. The aluminates of the alkali metals on standing slowly deposit aluminium hydroxide (cf. p. 378).

'Thenard's blue,' the blue mass obtained in qualitative analysis by heating alumina with cobalt nitrate on a charcoal block, is possibly *cobalt aluminate*, $\text{Co}(\text{AlO}_2)_2$ —though it may be a solid solution of CoO in Al_2O_3 .

The whole subject of aluminates is very complex, and little reliable evidence of their structure is so far available.

Aluminium chloride, AlCl_3 , or Al_2Cl_6 , can be prepared anhydrous by heating aluminium in a stream of carefully dried chlorine or hydrogen chloride. A suitable apparatus is shown in Fig. 71. The substance is volatile, and sublimes over (at 180°) directly into the wide-necked bottle in which it is to be preserved.

Aluminium chloride is very important in chemical industry and is manufactured to the extent of over 1,000 tons per annum. Calcined bauxite is mixed with coal and the mixture is made up into briquettes by the use of pitch or asphalt. The briquettes are strongly heated in furnaces through which a current of chlorine passes, when the chloride is formed according to the equation:



If aluminium chloride is made by dissolving the metal in hydrochloric acid, it can be crystallized out from the solution in the form of the colourless *hexahydrate*, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$. When this compound is heated, it is hydrolysed by its own water of crystallization and leaves a residue of alumina.

Anhydrous aluminium chloride is a white, hygroscopic solid which on heating sublimes at 183° . Vapour density determinations show

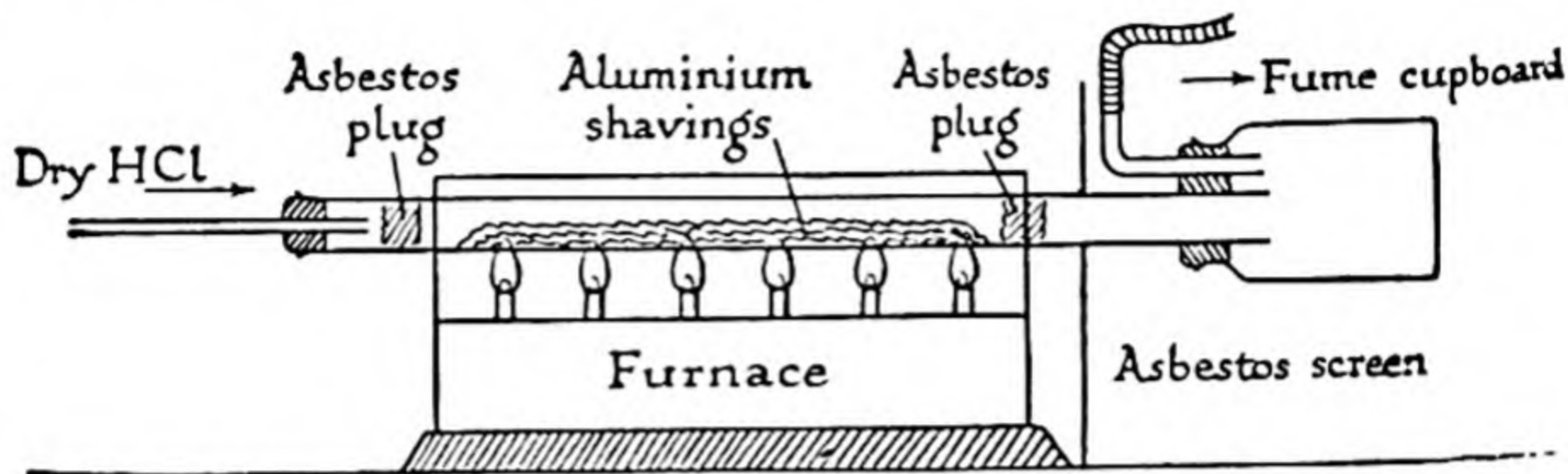
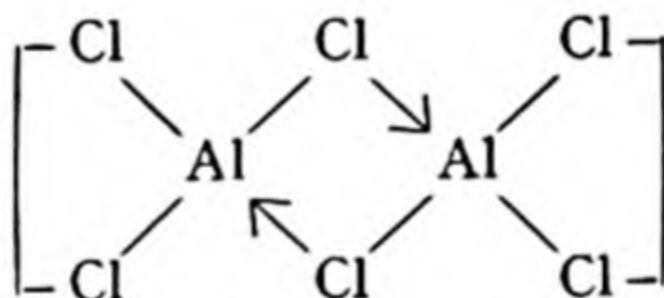


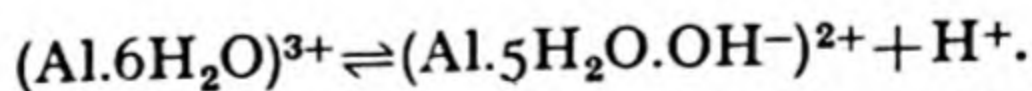
FIG. 71. PREPARATION OF ALUMINIUM CHLORIDE

that the molecules are Al_2Cl_6 below 400° , but on raising the temperature these dissociate into AlCl_3 molecules, dissociation becoming complete at about 800° . The constitution of the double molecule is believed to be

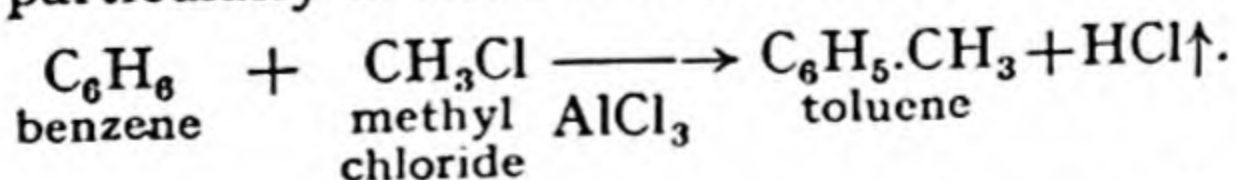


In organic solvents such as carbon tetrachloride, aluminium chloride exists as AlCl_3 . X-ray methods show that the *solid* chloride is ionic (Al^{3+} and Cl^-), but the solid bromide has been proved to have a structure corresponding to that shown for the chloride above.

Aluminium chloride dissolves in water, the solution reacting acid:

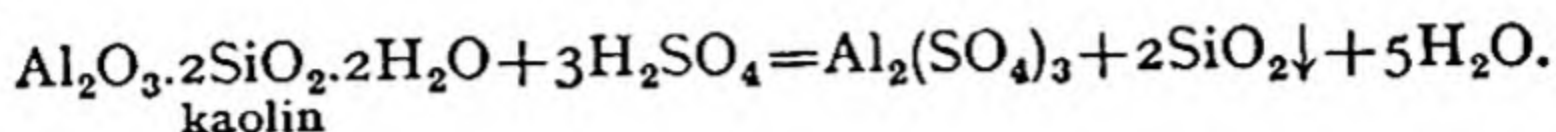


In organic chemistry anhydrous aluminium chloride is used as a catalyst, particularly in the FRIEDEL and CRAFTS reaction, e.g.:



Industrially its main use is as a catalyst in the 'cracking' of petroleum to form petrol.

Aluminium sulphate, $\text{Al}_2(\text{SO}_4)_3$. This salt is prepared by heating concentrated sulphuric acid with aluminium, though industrially an impure form is made by heating kaolin (china clay) with the acid:

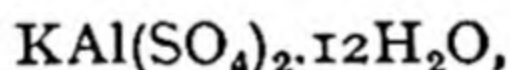


From aqueous solution it crystallizes with no fewer than eighteen molecules of water: $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$. The anhydrous salt may be obtained by cautiously heating the hydrate.

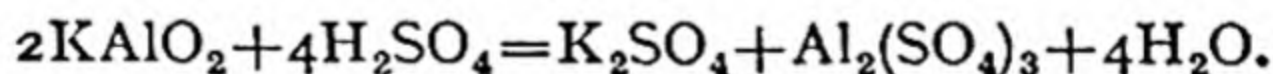
Alums. Ordinary alum is the most familiar example of a large number of similar compounds, to which it gives its name. The alums are salts of the general formula $\text{M}'\text{M}''(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, where M' is any of the univalent metals, Na, K, Rb, Cs, Ag, or Tl (or NH_4), and M'' is any of the tervalent metals Al, Cr, Fe, Mn, Co, Ga (and others). In solution, they give SO_4^{2-} ions and ions of both metals, but no complex ions; that is, they are true *double salts*, not complex salts.

They crystallize generally in octahedra, though occasionally in cubes. The octahedral crystals of different alums are isomorphous with one another, so that 'mixed crystals' can be obtained; moreover, since a crystal of any one alum will grow in a saturated solution of any other alum, composite crystals may be formed. Thus if a purple crystal of chrome alum, $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, is hung in a saturated solution of ordinary ('potash') alum, it grows by surrounding itself with a colourless layer of the latter.

Potash alum, or potassium aluminium sulphate,



can be made in the laboratory by dissolving aluminium in potassium hydroxide solution, and adding the requisite weight of sulphuric acid:



On evaporating the solution, crystals of the alum separate out.

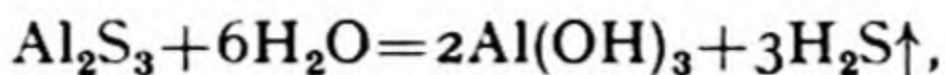
Commercially alum is made from the mineral *alunite*, or *alum-stone*, $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 4\text{Al}(\text{OH})_3$. This is roasted and extracted with water.

The *ferric alum* of the laboratory is usually ammonium ferric sulphate: $(\text{NH}_4)\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$.

Sodium alum differs from potash alum in being very soluble in water.

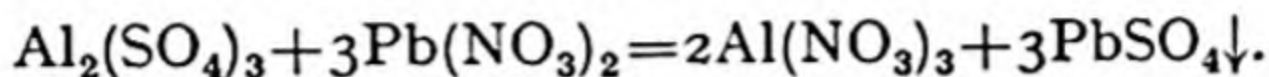
Aluminium sulphide, Al_2S_3 , can be prepared by direct synthesis; aluminium and sulphur are heated together in the proportion

demanded by the formula (54 Al : 96 S). It is hydrolysed completely by water:



so that when ammonium sulphide is added to a solution of an aluminium salt the *hydroxide*, not the sulphide, is precipitated.

Aluminium nitrate, $\text{Al}(\text{NO}_3)_3$, is best prepared by double decomposition between solutions of lead nitrate and aluminium sulphate:



It forms several hydrates, e.g. $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and decomposes on heating, yielding alumina.

USES OF ALUMINIUM AND ITS COMPOUNDS

The use of aluminium in thermit and the Goldschmidt process has already been mentioned. The metal itself, being resistant to corrosion by air and water, as well as non-poisonous and light, is widely used for domestic utensils such as kettles and saucepans. Light alloys, e.g. *duralumin* (Al, 95; Cu, 4; Mg, 0.5; Mn, 0.5 per cent), *magnalium* (Al, 95; Mg, 5 per cent), and Y-metal (about 92 per cent Al with varying proportions of Cu, Ni, and Mg), are important in the aeroplane industry. The pure metal is used for electric cables (with a steel core to give them the required strength), since, weight for weight, it is a better conductor than the much more expensive metal copper. Aluminium paint has merits, though perhaps not to an aesthete.

Aluminium salts, which in solution yield some (hydrated) hydroxide (p. 382), are employed in the dye industry. The hydroxide becomes attached to the fibre of the textile and there adsorbs soluble dye particles to form an *insoluble* coloured substance or 'lake.' The dye, which would otherwise be removed by washing, is thus rendered fast; it has, so to speak, 'bitten' the fabric, which is why the aluminium salts employed (e.g. the acetate) are known as *mordants* (Latin, *mordere*, to bite).

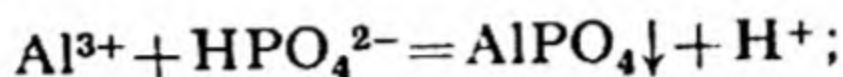
Porcelain, *earthenware*, *bricks*, *terra cotta*, *stoneware*, and *fireclay* are all made from various grades of clay, which is essentially $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. The purest form of clay is 'china clay,' or kaolin.

The 'blue-bag' — that popular weapon of the washerwoman — contains *ultramarine*, a complex substance of composition $\text{Na}_4\text{Al}_3\text{Si}_3\text{S}_2\text{O}_{12}$ made by heating a mixture of kaolin, sodium carbonate (or sulphate), sulphur, and charcoal. Linen of a yellowish tinge appears white if rinsed in a solution of ultramarine and then dried; but lavish use of the blue-bag does not mask inefficient washing.

Tests for Aluminium.

Solutions of aluminium salts give with

- (a) ammonia solution: white precipitate of Al(OH)_3 , insoluble in excess;
- (b) sodium or potassium hydroxide: white precipitate of Al(OH)_3 , soluble in excess;
- (c) disodium phosphate: gelatinous precipitate of aluminium phosphate, insoluble in acetic acid but soluble in hydrochloric acid:



- (d) (*spot test*) alizarin turned violet by the action of ammonia: a red 'lake.'

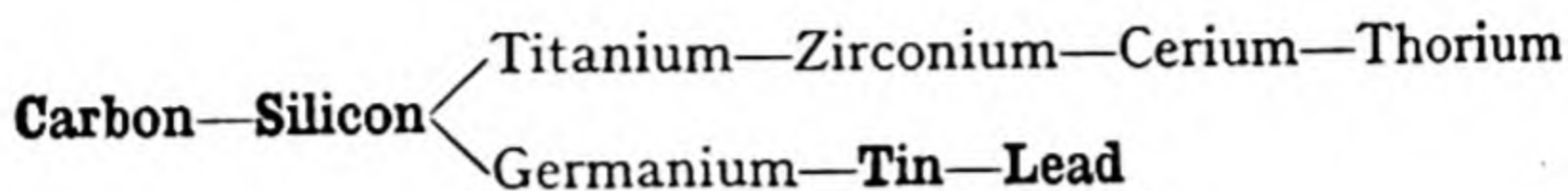
COMPARATIVE EXERCISES

1. Tabulate the chief points in which boron and its compounds (a) resemble, and (b) differ from, aluminium and its compounds.
2. After reading Chapter XXXI, compare and contrast the properties of ferric compounds with those of aluminium.
3. After reading Chapter XXVII, compare and contrast the properties of boron and boron compounds with those of silicon and silicon compounds.

CHAPTER XXVII

GROUP IV

CARBON, SILICON, TIN, LEAD



CARBON, C

Atomic number : 6. *Atomic weight* : 12.011. *Specific gravity (graphite)* : 2.3. *Melting-point* : 3,570°. *Boiling-point* : 4,200° (?)

History. In the forms of charcoal and soot, carbon must have been known since the discovery of fire. The Romans manufactured carbon-black (for inks and black pigments) by burning resin in a limited supply of air. They were probably also acquainted with *graphite*, which, however, they confused with lead and molybdenum sulphides. *Diamonds* were familiar to, and highly prized by, some ancient peoples, though specimens were rare except in India. PLINY well describes the diamond as a colourless and transparent crystal, having six angles, polished faces, and terminating like a pyramid in a sharp point; or also pointed at the opposite extremities, as though two many-sided pyramids were joined together at their bases. He also says that small diamonds 'are in request with gem-engravers, and are mounted in iron tools, their being no substances so hard that they cannot hollow out with the greatest ease.'

In 1604 DE BOOT expressed the opinion that the diamond was of a fiery and sulphureous nature. A century later SIR ISAAC NEWTON conjectured it to be inflammable, on account of its high refractive index, and shortly afterwards AVERANI demonstrated the combustion of a diamond before the GRAND DUKE COSMO III of Tuscany. In 1775 LAVOISIER showed that the product of combustion was carbon dioxide, and in 1797 TENNANT proved that the ratio by weight of carbon dioxide to diamond was 44 : 12, and that therefore the diamond was pure carbon. A similar proof of the nature of graphite was made by MACKENZIE in 1800.

Occurrence. Carbon occurs as the allotropes graphite and diamond, which are considered below. Coal (p. 390) contains some free carbon, and the total percentage of the free and combined element in it may be very high. Carbon also occurs in carbonate

rocks (e.g. *limestone, chalk, marble*, CaCO_3 , and *dolomite*, $\text{CaCO}_3 \cdot \text{MgCO}_3$); in temporarily hard water as *calcium bicarbonate*, $\text{Ca}(\text{HCO}_3)_2$, or the similar salts of magnesium and ferrous iron; in petroleum, which is mainly a mixture of *hydrocarbons* (i.e. carbon hydrides); as *carbon dioxide* in the air (0.03–0.04 per cent by volume); and as the fundamentally essential element in all living matter. Charcoal, gas-carbon, coke, and lampblack are artificially prepared impure forms of carbon.

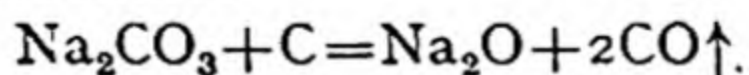
Diamond. The chief diamond fields are in South Africa, South America, and India, though diamonds are also found in Australia and other countries. In South Africa they most frequently occur in funnel-shaped pockets of a blue earth or 'blue ground,' possibly of volcanic origin. The natural stones have to be cut and polished before use as jewels.

Artificial production of diamonds has proved an extremely difficult task, and cannot yet be described as fully successful. In a series of experiments, of which a brief preliminary account has appeared (1955, *Nature*, vol. 176, p. 51), carbon, apparently with some fluxing material, was submitted to a pressure of 10^5 atm. at temperatures above 2300° . Crystals were obtained weighing up to 0.05 gm. with 1 mm. edge, and were found to possess most of the properties of natural diamond, but contained only 86 per cent of carbon.

Diamond is the hardest mineral known, and will scratch all other minerals; it therefore stands first on MOHS'S *scale of hardness*, which is a list of ten minerals each of which will scratch all those below it: *

- | | |
|-------------|-------------|
| 1. Diamond | 6. Apatite |
| 2. Corundum | 7. Fluorite |
| 3. Topaz | 8. Calcite |
| 4. Quartz | 9. Gypsum |
| 5. Felspar | 10. Talc |

Diamond has a high refractive index (2.4), and a higher specific gravity (3.52) than graphite (2.3). It can easily be distinguished from imitation or 'paste' diamond by the fact that it is transparent to X-rays; 'paste' is opaque. Chemically diamond is extremely unreactive, though it is gradually oxidized to carbon monoxide by fused sodium carbonate:



and to carbon dioxide by a hot mixture of potassium dichromate and concentrated sulphuric acid. Its ignition point in air is about 900° ; on combustion it yields carbon dioxide with a minute residue of ash (chiefly silica).

* F. Mohs (*not* Mob) was a German professor of mineralogy (1773–1839).

Graphite.—Graphite is used in pencils ('black-lead'); hence its name, from the Greek *graphō*, 'I write.' It occurs naturally in Ceylon, Russia, and central Europe, and workable deposits formerly existed at Borrowdale, Cumberland, but these are exhausted or no longer profitable. Graphite is now prepared artificially by the ACHESON electrothermic process. Anthracite, or the purest commercial coke, is heated strongly in an electric furnace in the absence of air, and is converted into graphite of good quality.

Graphite is an opaque greyish-black crystalline solid, with a greasy feel, and readily flakes into thin hexagonal plates. It is a good conductor of electricity. Chemically it is more re-

active than diamond; thus it combines with potassium to form the unstable compounds KC_8 and KC_{16} , and is converted by a mixture of potassium chlorate and nitric acid into the greenish-yellow *graphitic oxide*, C_3O .^{*} Concentrated sulphuric acid, in the presence of strong oxidizing agents, converts graphite into a bluish substance known as 'blue graphite'; this is a bisulphate of approximate composition $C_{24}HSO_4$. With fused sodium carbonate, graphite slowly yields carbon monoxide (cf. diamond).

^{*} Actually the potassium and oxygen atoms are held between *sheets* of carbon atoms, and the composition of graphitic oxide is variable.

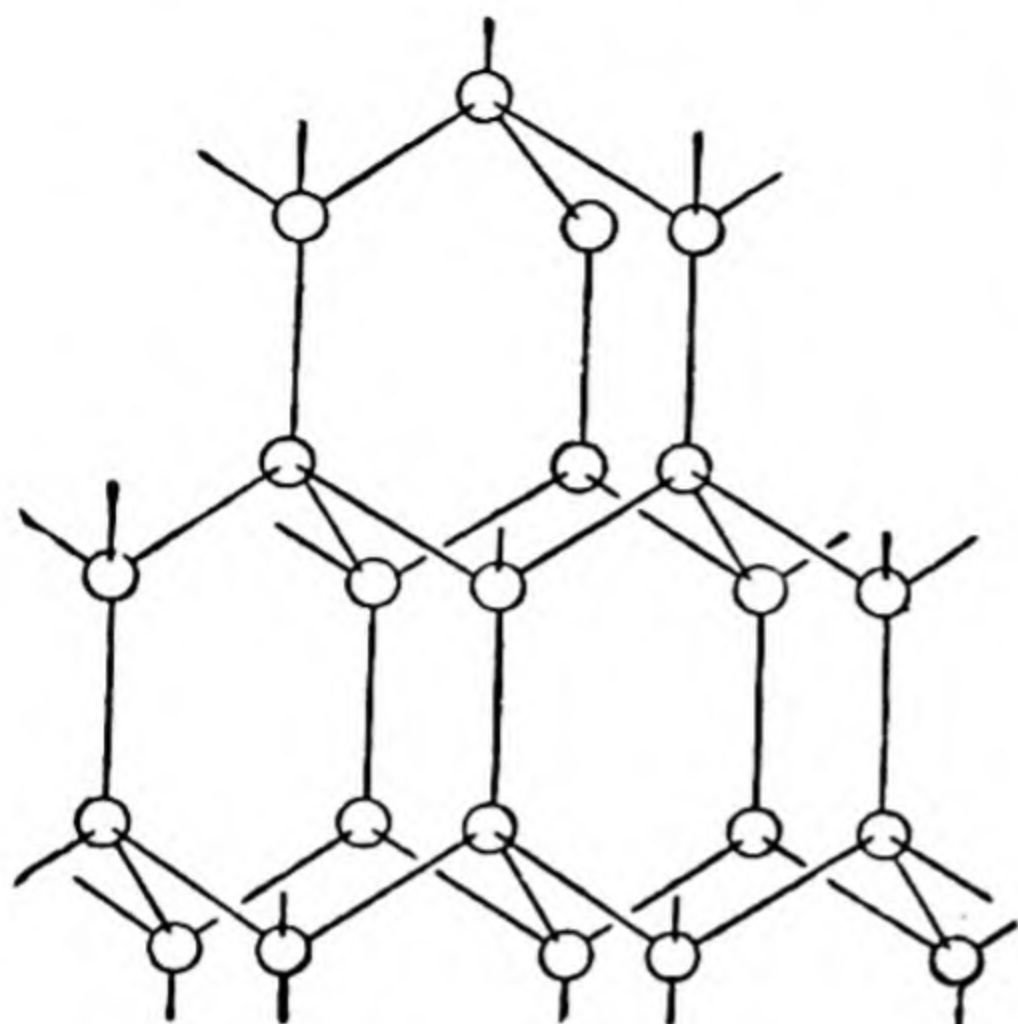


FIG. 72. STRUCTURE OF DIAMOND

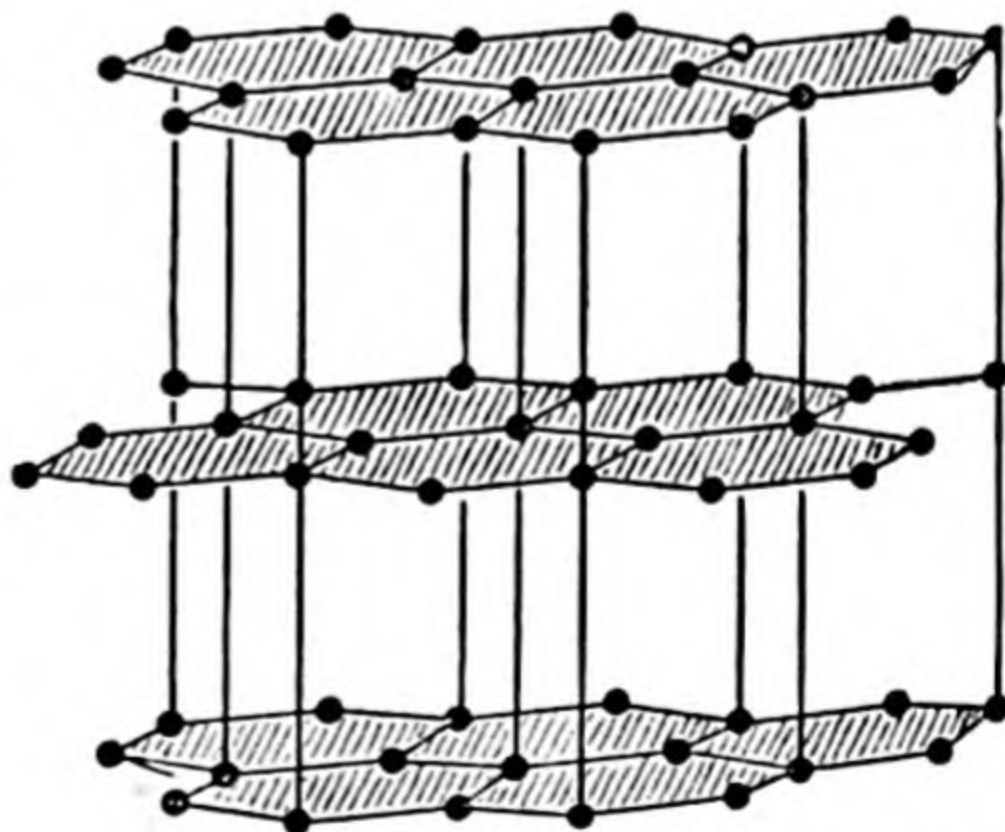


FIG. 73. STRUCTURE OF GRAPHITE

One of the principal uses of graphite is as a lubricant, an application elegantly explained by the structure of its crystals. Fig. 72 shows that in diamond the carbon atoms are arranged tetrahedrally. This is a very stable arrangement, in agreement with the hardness and chemical unreactivity of diamond. In graphite, however, (Fig. 73), the atoms are arranged in hexagonal sheets comparatively widely separated from one another,* and this structure gives an easy shear or displacement parallel to the plane of the hexagons. The lubricating power of graphite, which depends upon the ease of this displacement, is increased if the graphite is used in the form of colloidal solutions in water, mineral oil, or castor oil. Such colloidal graphite is marketed by the Acheson Company under the names of *aquadag*, *oildag*, etc.†

Graphite is also used for making refractory crucibles, fixed and variable electrical resistances, electrodes, etc., and as a coating for non-conducting materials upon which metals are to be deposited electrolytically. The 'lead' in pencils is a mixture of graphite and clay.

'Amorphous' Carbon. Coke, soot, and various forms of charcoal are classed together as 'amorphous' carbon, since they have no obvious crystalline structure. They are, however, probably all graphitic, and some of them have been definitely proved to consist of minute crystals of graphite.

Coke is the residue left in the retorts after the destructive distillation of coal in the manufacture of coal-gas (p. 392). It contains 80–85 per cent of carbon.

Gas-carbon is also produced during the above operation, and forms a hard lining within the retorts. It is purer than coke, and conducts electricity well. It is used for making electrodes, e.g. in arc-lamps.

Charcoal is obtained by the partial combustion of wood in an insufficient supply of air, and by subjecting wood to destructive distillation. It is a very porous substance, and readily absorbs certain gases, colouring-matter, and volatile liquids. The absorption is greatly enhanced by heating the charcoal in superheated steam, when 'active carbon' results. Active carbon made from coco-nut shell and peat is used in gas-masks, and in the recovery of the vapours of volatile solvents, e.g. from the air in dry-cleaning works. *Animal charcoal*, or *bone black*, is obtained by heating bones in the absence of air, and consists of some 10 per cent of carbon with 90 per cent of calcium phosphate. Its principal use is in the decolorizing of coloured solutions that should be colourless, e.g.

* X-ray measurements show that the distance between the planes is about $2\frac{1}{2}$ times as great as the side of the hexagon.

† D.a.g.=deflocculated Acheson graphite.

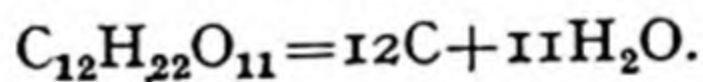
raw sugar syrup. The sugar solution is passed down a tower containing animal charcoal or active carbon, and emerges at the bottom colourless.

Lampblack. Lampblack, or soot, is a very finely divided form of carbon, and though the commercial grades may contain oil and grease as impurities, it can be obtained in a high state of purity. It is manufactured by burning petroleum, naphthalene, the natural gas of oil-fields, and other carbonaceous materials, in specially constructed furnaces, the supply of air being limited to the minimum required for combustion. The soot passes along tubes made of sheepskin, canvas, or coarse cloth, whence it is shaken off after the operation is complete. If better qualities are required, the crude lampblack is subjected to a second partial combustion, and the process is repeated as often as necessary.

More than half the world's production of lampblack is used in the motor-tyre industry, since rubber containing 25 per cent of lampblack is about four or five times as resilient and resistant as pure rubber. Much lampblack is also used in the manufacture of printer's ink, while smaller—but still considerable—quantities are employed in making gramophone records, carbon copying-paper, ebonite articles, carbon electrodes, and black pigments.

The application of chimney soot to garden soil is beneficial mainly because it usually contains up to 7 per cent of ammonia as ammonium compounds, derived from the coal.

Sugar carbon is one of the purest forms of carbon. Pure sucrose (i.e. cane or beet sugar) is charred by heating it in the absence of air:



The residual carbon may contain traces of hydrogen and oxygen, which are removed by heating it in successive streams of hydrogen (to remove oxygen), chlorine (to remove hydrogen), and hydrogen (to remove chlorine remaining after the last treatment).

Properties. 'Amorphous' carbon is a black solid which on heating in air or oxygen ignites at a much lower temperature (about 400°) than graphite or diamond. The product of free combustion is carbon dioxide; in a limited supply of air or oxygen carbon monoxide is formed. Both products are strongly exothermic, so that carbon is a good reducing agent, and is used as such in industrial chemistry as well as in the laboratory.

If strongly heated in hydrogen, carbon forms various hydrocarbons, e.g. *methane*, CH_4 , and *acetylene*, C_2H_2 . It also combines directly with sulphur vapour, forming *carbon disulphide*, CS_2 , and with many heated metals, forming *carbides*, e.g. CaC_2 , Al_4C_3 .

Coal. Though coal is often described as an impure form of carbon, it actually contains very little of the free element, but consists

mainly of a complex colloidal mixture of compounds of carbon, hydrogen, and oxygen. Nitrogenous compounds are also present, as well as small quantities of compounds of other elements, particularly phosphorus and sulphur. Such a composition indicates that coal is of vegetable origin, a conclusion confirmed and indeed anticipated by the observation of fossil plants in coal seams.

The coal beds were formed about three hundred million years ago, in the Carboniferous Age, when vast forests flourished in a damp and uniformly warm climate. These forests were composed chiefly of *Pteridophyta*, i.e. plants resembling our present-day ferns, horse-tails, and club-mosses; the prehistoric pteridophytes were, however, very much larger on the whole than their modern representatives. A fossil *Lepidodendron*, for instance, discovered in a coal-mine, was found to measure no less than 114 feet from its base to its first branches, while living members of the same family are humble plants of moss-like habit.

Coal is the final product of the decay and fossilization of this luxuriant vegetation, the successive stages being perhaps approximately represented by (a) a kind of peat, (b) lignite, or 'brown coal,' (c) bituminous coal, such as is used for making coal-gas, and (d) anthracite. The process may have taken place on the actual site of the swampy forest, or the vegetable debris may have been carried away by flood and drifted together elsewhere; in some cases examination of the seams shows that the material was probably water-borne, while in others the evidence appears to be conclusive that it was formed in the place it now occupies. The British coalfields almost certainly arose *in situ*.

The agents of the decay suffered by the Carboniferous vegetation were bacteria, while heat, and the pressure of the overlaying strata deposited later, completed the conversion of the decayed material into the hard, rocky state of coal. The exact nature of the changes undergone by the plant remains is gradually being made clear by the study of individual varieties of coal, and by such other methods as the extraction of coal with solvents (e.g. pyridine and benzene) under pressure, and an investigation of the products of its regulated oxidation.

Wood is composed of substances known as ligno-celluloses, i.e. compounds of cellulose, $(C_6H_{10}O_5)_n$, with a body of uncertain composition called lignone or 'lignin.' From the researches of BONE and his co-workers, it seems likely that coal has been derived mainly from the lignin part of the wood. Cellulose upon mild oxidation yields almost entirely carbon dioxide and oxalic acid, while lignin yields a considerable quantity of acids derived from benzene, C_6H_6 . When coal is similarly oxidized, acids of the latter type are always formed, and in the case of anthracite they may represent as much

as 50 per cent of the original carbon. From these results, BONE concludes that, in the formation of coal, lignin has taken the chief part, the cellulose having mainly disappeared. Other investigators take different views, and the problem must be regarded as still far from a final solution.

Peat. It was stated above that the first stage in the formation of coal probably resembled peat. Peat, however, is composed of the decayed remains of mosses and aquatic flowering plants such as reeds and sedges, and thus differs in origin from coal. Large quantities of peat are found in many parts of the world; it has, for example, been estimated that the peat areas in the Union of Soviet Socialist Republics amount to nearly 70,000 square miles, and in Canada to some 37,000 square miles. Smaller deposits occur in Great Britain and in Ireland, and in the latter country form an important source of fuel. The composition of peat is very variable, but an average specimen dried in the air has a calorific value of between 6,000 and 9,000 B.Th.U. per lb., and contains about 60 per cent of carbon.

Lignite, or brown coal. This is mined mainly in Germany, which produces some 150,000,000 tons annually. It contains about 67 per cent of carbon, 24 per cent of hydrogen and oxygen, and 9 per cent of ash.

Bituminous coal is the ordinary domestic variety. It contains, on an average, 88 per cent of carbon.

Anthracite, or hard coal, may contain as much as 96 per cent of carbon, though the usual content is about 94 per cent.

Coal-gas. That coal gives off an inflammable gas when heated has been known for centuries. The first man to make practical use of the discovery, however, was WILLIAM MURDOCK, who in 1792 illuminated his house at Redruth, Cornwall, with it. Finding the results eminently satisfactory, he tried to interest business men in the system, and called to see JAMES WATT (of the flourishing firm of BOULTON & WATT, Birmingham). Watt might have taken little account of his visitor, but for the fact that Murdock dropped his hat, which made an unexpectedly noisy impact with the floor. Watt's curiosity led him to inspect the hat more closely, and he found that it was turned out of a solid block of wood. Feeling that a man who was ingenious enough to make his own hat out of such unpromising material must, at least, not be talking through it, Watt listened to Murdock's suggestion, and in 1802-3 the works of Boulton & Watt was lighted by coal-gas.

When coal is strongly heated in the absence of air, the following products are formed:

- | | |
|-------------|-----------------------------------|
| 1. Coal-gas | 3. Gas-liquor (ammoniacal liquor) |
| 2. Coal-tar | 4. Coke. |

The composition of coal-gas is roughly as follows:

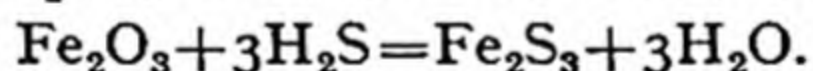
<i>Hydrogen</i>	50	per cent
<i>Methane, CH₄</i>	32	„
<i>Carbon monoxide</i>	8	„
<i>Ethylene, C₂H₄</i>	4	„
<i>Nitrogen</i>	6	„

The actual composition varies with the composition of the coal and the temperature at which it is heated.

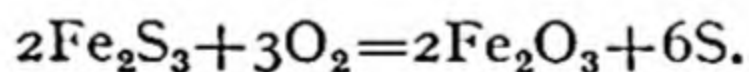
Of these gases, all except nitrogen are inflammable. Hydrogen, methane, and carbon monoxide burn with bluish, non-luminous flames. The luminosity of ordinary coal-gas is mainly due to the ethylene, which burns with a highly luminous flame.

The distillation of the coal is carried out in fire-clay retorts, D-shaped in section, mechanically charged, and heated by the combustion of producer-gas (p. 396). After leaving the retorts, the gas passes into an overhead hydraulic main, which is partly filled with water to act as a seal, thus allowing each retort to be opened separately without loss of gas. A good deal of the tar, and some of the ammonia, condense in the hydraulic main.

The gas then passes into a series of water-cooled condensers, where the ammoniacal liquor and more tar condense and run down to the tar-well (Fig. 74). The gas is drawn along and propelled through the washing and purifying plant by the exhausters, which are steam-driven rotary pumps. In the scrubbers, which commonly consist of towers packed with coke over which water trickles, the final traces of ammonia are dissolved, and the gas then enters the purifiers. These are large cast-iron vessels filled with trays carrying moist ferric oxide, the purpose of which is to remove hydrogen sulphide:

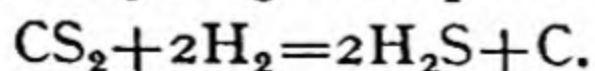


The ferric oxide can be recovered by exposing the Fe_2S_3 to air and moisture:



When the sulphur content of the material has become sufficiently high, the 'spent oxide' is used as a source of sulphur dioxide in sulphuric acid manufacture. In modern practice, a little air is mixed with the coal-gas before it enters the purifiers, and the regeneration of the ferric oxide then takes place continuously.

After leaving the purifiers, the gas still contains carbon disulphide as an impurity. This is removed by the use of a nickel catalyst at 420° , which converts the carbon disulphide and some of the hydrogen of the gas into hydrogen sulphide and carbon:



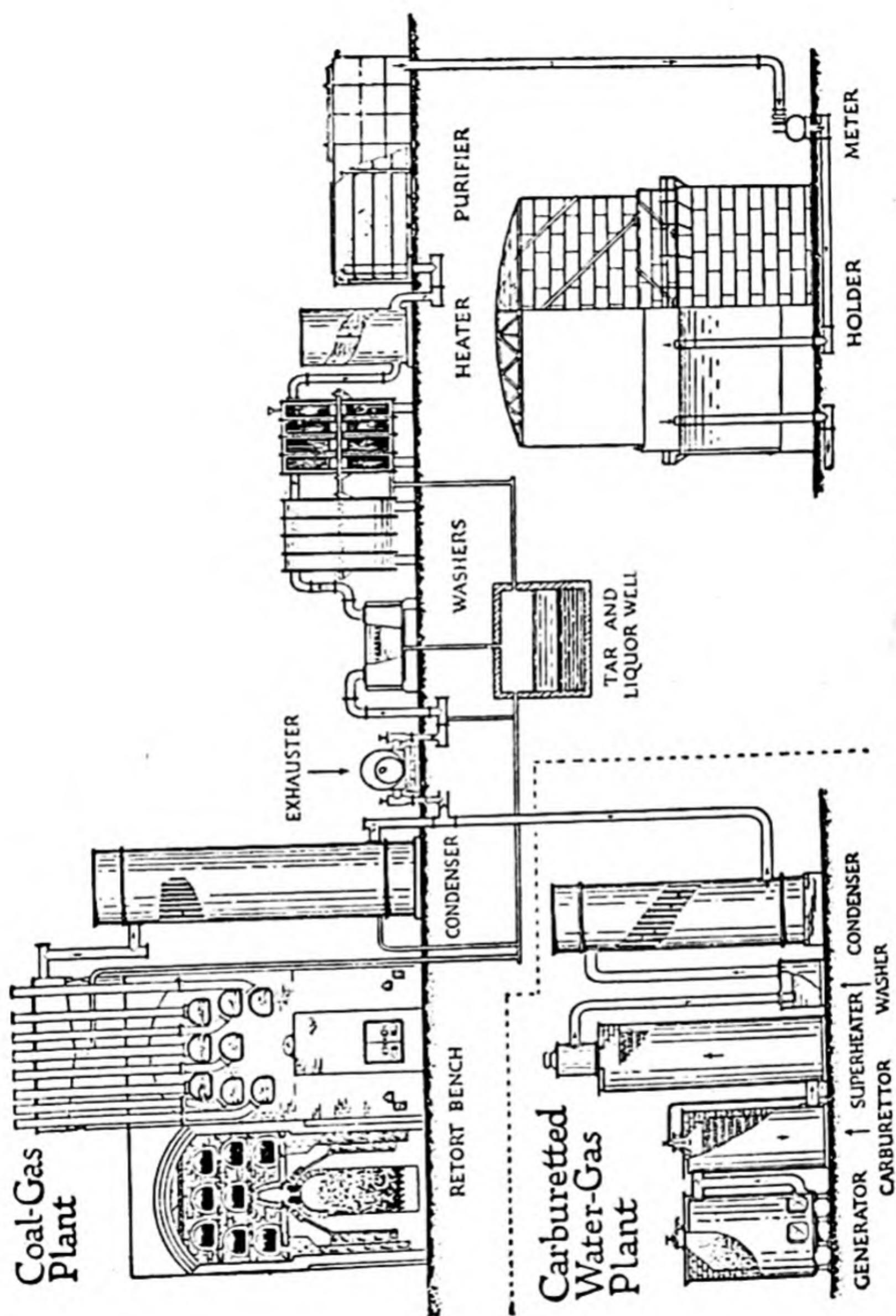


FIG. 74. DIAGRAM OF A COAL-GAS PLANT

The hydrogen sulphide is absorbed in the ferric oxide and the carbon is burnt out of the catalyst chamber at suitable intervals.

Finally, the valuable impurity *benzene*, C_6H_6 , is removed by passing the gas through active carbon (p. 389). This absorbs the benzene, which is afterwards recovered by distillation.

Coke-ovens. When the primary object of distilling coal is to get coke rather than coal-gas, the temperature employed is much

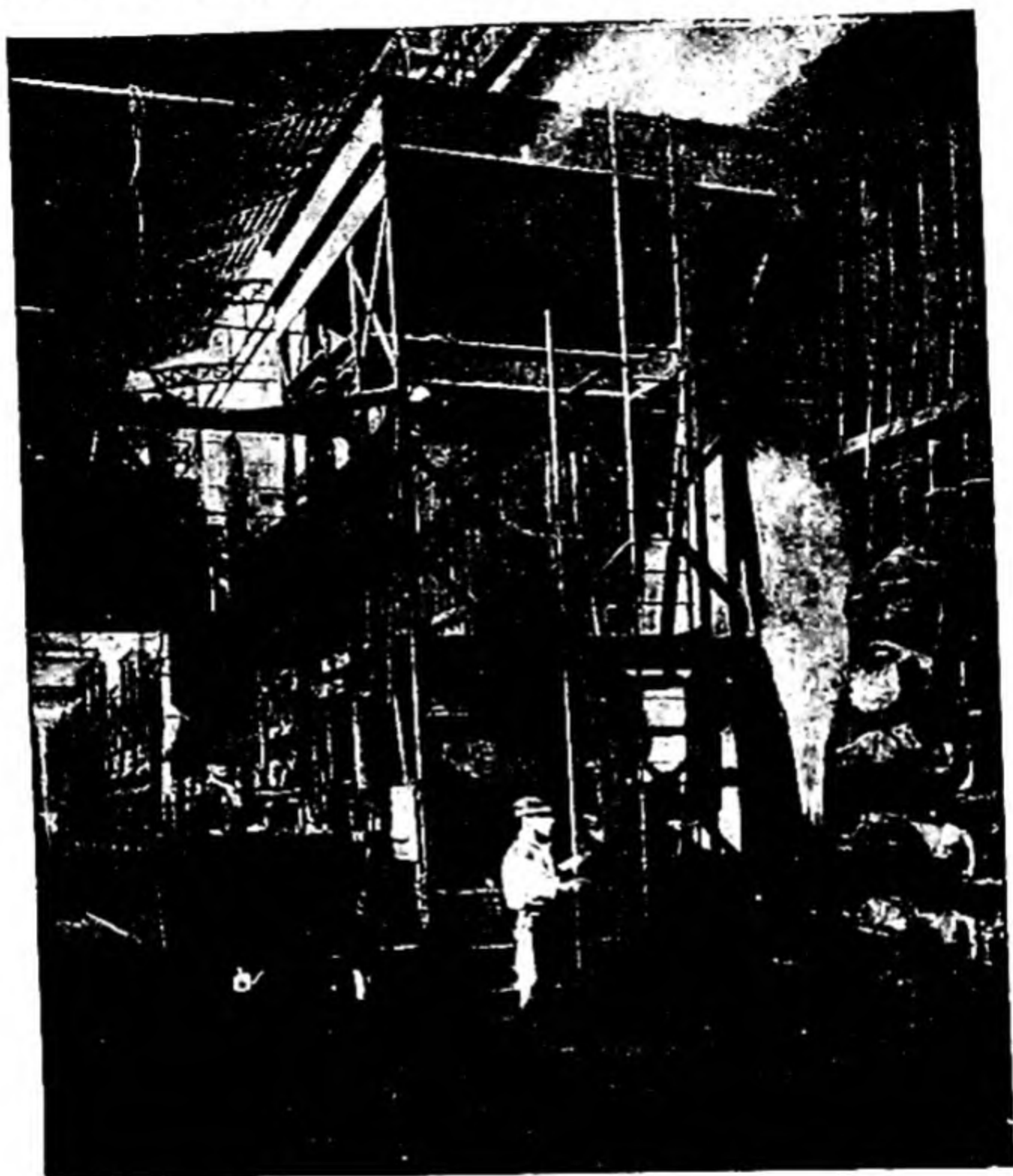


FIG. 75. CHARGING RETORTS

higher. Tar, ammonia, and benzene are recovered, and nearly half the coke-oven gas is used to heat the retorts. Some of the rest is sold to gas companies, but much is burnt to waste.

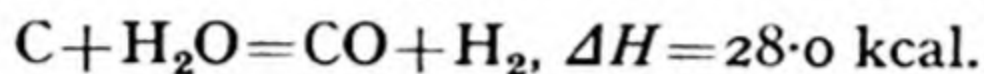
Low-temperature Carbonization. If coal is heated at 600° , instead of at $1,000^{\circ}$ as is usual in gas-works, a smaller yield of gas is obtained, but the solid residue, 'coalite,' is a smokeless fuel. The tar is also of a more useful kind, and oils suitable for combustion in internal combustion engines are formed as a further by-product, to the extent of some 3 gallons per ton of coal.

Producer-gas. This is a mixture of carbon monoxide and nitrogen prepared by burning coke in a supply of air insufficient to convert it into carbon dioxide. The reaction is strongly exothermic:



and if the gas is to be used in furnaces it is burned immediately after production, so that its heat of formation is not wasted. If, however, it is required for internal combustion engines it must be washed before use, and there is then considerable loss of heat.

Water-gas. Water-gas is a mixture of carbon monoxide and hydrogen (with small quantities of carbon dioxide and nitrogen), made by driving steam through incandescent coke:



This operation, called the 'run,' is endothermic, and the temperature of the remaining coke quickly falls. When it has reached a red heat, the steam is switched off and a 'blow' of air is substituted for it. Producer-gas is now formed, and the coke is raised to a white heat. 'Run' and 'blow' thus alternate with one another, fresh coke being introduced as required.

The water-gas so obtained burns with a blue flame and is therefore called 'blue' water-gas. In this form it is used as a source of hydrogen (BOSCH process, p. 275) and of synthetic methyl alcohol. To supplement the supply of coal-gas, the water-gas is 'carburetted' by passing it through brickwork superheaters (heated by producer-gas from the 'blow') into which paraffin oil is introduced. The oil is decomposed by the heat into gaseous hydrocarbons, and the water-gas thus burns with a luminous flame like coal-gas. The calorific (i.e. heat-producing) power of water-gas is less than that of coal-gas, but since gas is sold on the basis of its heating capacity and not by volume the interests of the consumer are safeguarded.

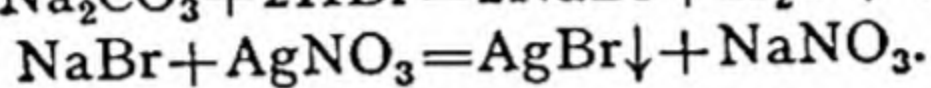
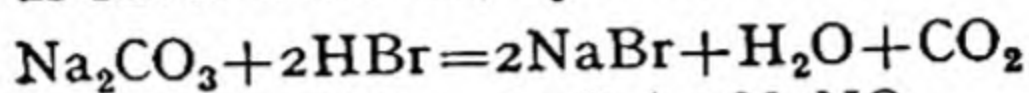
Semi water-gas is a mixture of producer-gas and water-gas made by conducting run and blow simultaneously. It contains about 20 per cent of nitrogen, 40 per cent of hydrogen, and 28 per cent of carbon monoxide (see further p. 431).

Atomic Weight. The determination of the atomic weight of carbon has been carried out by many investigators using a wide variety of methods. The most obvious method is to take a known weight of graphite or diamond, burn it completely in a current of oxygen, and find the weight of carbon dioxide produced; the ratio carbon : oxygen is thus determined directly. Experiments of this kind were carried out by DUMAS, FRIEDEL, ERDMANN and MARCHAND, ROSCOE, and others. In one investigation Roscoe burned 6.4406 gm. of Cape diamonds and obtained 23.6114 gm. of carbon dioxide,

\therefore 17.1708 gm. of oxygen combine with 6.4406 gm. carbon,
hence 8.0000 gm. of oxygen combine with 3.001 gm. carbon.

The equivalent of carbon is thus 3.001 and the atomic weight 4×3.001 or 12.004. The results of other works were in fairly close agreement.

A second method was employed in 1915 by RICHARDS and HOOVER, who neutralized carefully purified sodium carbonate with hydrobromic acid, and afterwards precipitated the bromine from the sodium bromide as silver bromide, by the addition of silver nitrate:



They were thus able to calculate the ratio $\text{Na}_2\text{CO}_3 : \text{Ag}$ and obtained the value $C = 12.005$.

The method of limiting density (p. 29), using carbon monoxide or methane, gave results varying from 12.003 to 12.01, the last figure being obtained by WHYTLAW GRAY and WOODHEAD in 1933.

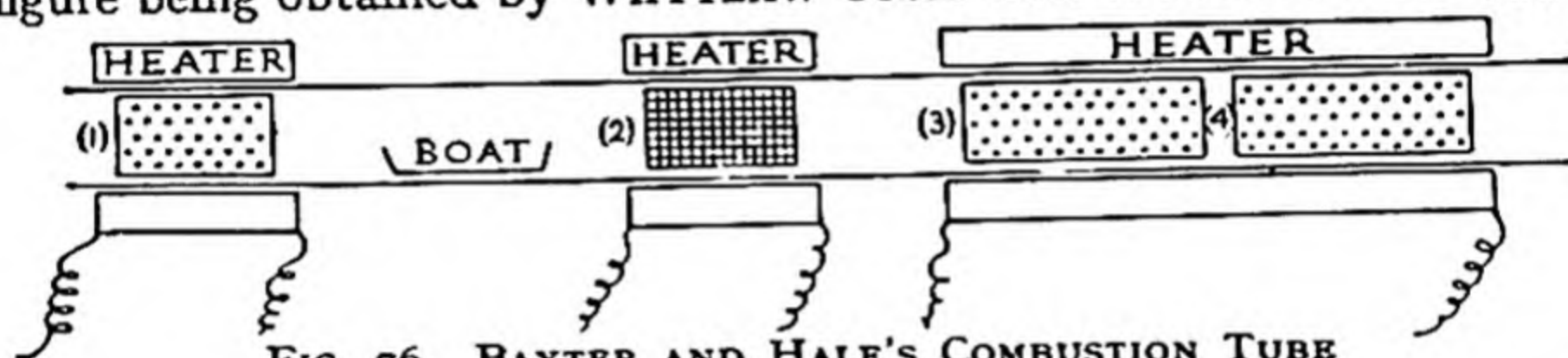


FIG. 76. BAXTER AND HALE'S COMBUSTION TUBE

Confirmation of the value 12.01 was provided by the work of BAXTER and HALE in 1936, the procedure they adopted being shortly as follows:

The practical difficulties of preparing absolutely pure carbon are very great, and natural carbon (e.g. graphite and diamond) always contains impurities; hence the determination of the ratio $C : \text{CO}_2$ cannot be carried out directly to the desired degree of accuracy if the element itself is used as the starting-point. Certain aromatic hydrocarbons, however, can be obtained in a high state of purity, and if such a hydrocarbon of known formula is completely oxidized, the $C : \text{CO}_2$ ratio can be calculated from the weight of substance taken and the weight of carbon dioxide formed. Moreover, if the weight of water produced at the same time is also determined, it is not necessary even to assume the formula of the hydrocarbon. Baxter and Hale therefore burned a weighed amount of the hydrocarbon 'in pure oxygen and both the carbon dioxide and the water formed were collected and weighed. From the weight of water the weight of hydrogen was calculated. The difference between the weight of hydrocarbon and the weight of hydrogen yields the weight of carbon in the original material, and from the weights of car-

bon and carbon dioxide the atomic weight of carbon may be calculated.'

One of the hydrocarbons selected was chrysene, $C_{18}H_{12}$. This was carefully purified by repeated recrystallization from pure tetrachloroethane and subsequently from pure benzene, followed by two distillations in high vacuum and two further recrystallizations from benzene. The combustion apparatus consisted of a thick quartz tube containing (1) a platinum basket filled with platinized quartz chips, (2) a roll of platinum gauze at dull redness (650°), (3) a roll of perforated platinum foil, and (4) a perforated platinum basket filled with copper oxide, both (3) and (4) being kept at 800° . The object of the platinum was to catalyse the oxidation of the hydrocarbon, while the copper oxide was inserted as a guard against a possible deficiency of oxygen. Heating was effected electrically.

The oxygen used for the combustion was prepared from air by liquefaction and was purified by passage through or over the following substances successively: potassium hydroxide solution, hot copper oxide, potassium hydroxide solution, solid potassium hydroxide, hot platinum, amalgamated copper gauze, solid potassium hydroxide, and phosphorus pentoxide.

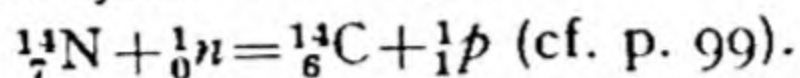
To prepare the chrysene for weighing, about 3 gm. was placed in a weighed platinum boat and heated just to the melting-point in a current of nitrogen. The boat with its contents was then allowed to cool in nitrogen and to stand in a desiccator for some time, after which the weight of the material was found. The combustion tube was swept out with oxygen for half an hour, and the boat with the chrysene was then introduced into the space between the platinum basket (1) and the roll of platinum gauze (2). The water formed was collected as liquid water in a cooled and weighed absorption tube of special design, while the carbon dioxide was absorbed in a weighed tube containing asbestos impregnated with fused sodium hydroxide. Buoyancy and other corrections were applied to correct the weights actually observed, the oxygen left in the absorption apparatus being swept out with a current of the same specimen of pure dry air as that with which the tubes were originally filled.

The results of four determinations were as follows:

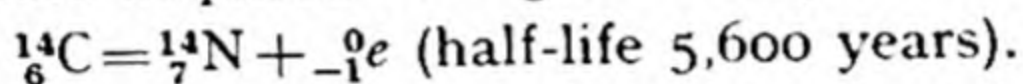
<i>Weight of chrysene in gm.</i>	<i>Water formed in gm.</i>	<i>Hydro- gen in gm.</i>	<i>Carbon in gm.</i>	<i>Co₂ in gm.</i>	<i>Oxygen in gm.</i>	<i>Ratio C : O₂</i>	<i>Atomic weight of carbon</i>
2.78044	1.31209	0.14680	2.63364	9.65247	7.01883	0.375225	12.007(2)
2.69258	1.27609	0.14277	2.54981	9.34368	6.79387	0.375310	12.009(9)
2.97782	1.41063	0.15782	2.82000	10.33447	7.51447	0.375276	12.008(8)
2.99649	1.41913	0.15877	2.83772	10.39870	7.56098	0.375311	12.010(0)
					<i>Average</i>	0.375281	12.009(0)

Hence it seems that the atomic weight of carbon is 12.01; and this is found to be in good agreement with the relative abundance in which the isotopes C^{12} and C^{13} occur in carbon. (The radioactive isotope, C^{14} , is prepared artificially.)

Radio-carbon and the Dating of Archeological Materials. Neutrons from outer space are absorbed at about 30,000 feet altitude by atmospheric nitrogen, which is thereby transmuted into radio-carbon, ^{14}C , by the ejection of a proton:



The radio-carbon atoms so formed burn to carbon dioxide before reaching the earth. Through photosynthesis all plant life comes to contain some ^{14}C , and hence all animal life. Carbonate and bicarbonate in the sea exchange with active carbon dioxide in the atmosphere. Radio-carbon thus becomes diffused throughout terrestrial matter. As soon as wood or bone ceases to be part of living plants or animals the absorption of radio-carbon ceases, and that which has been acquired during life decays at a known rate:



The terrestrial ratio of ^{14}C to ^{12}C is extremely minute and the *beta*-activity of radio-carbon is intrinsically feeble, so that very sensitive apparatus is needed to detect it; but such difficulties have been successfully overcome, and it is becoming usual for carbon-containing prehistoric objects to be dated by measuring the extent of the radioactive decay of their radio-carbon. Materials from Stonehenge were found to have an age of 3,600 years, in very close agreement with an estimate of the Astronomer Royal based upon entirely separate data.

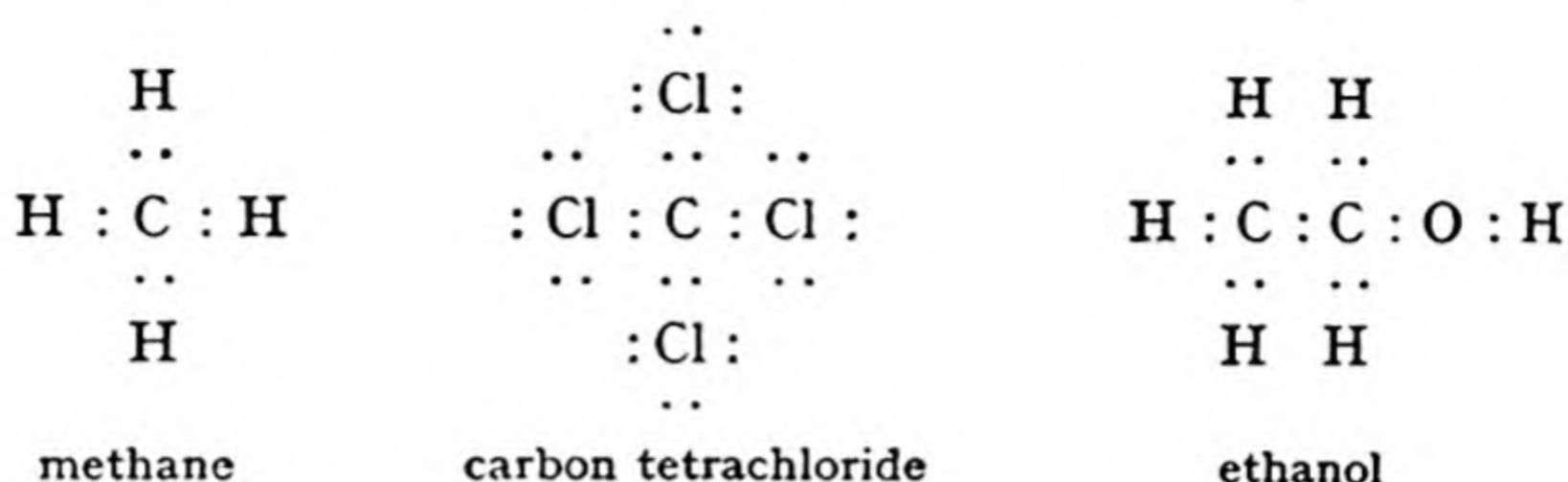
COMPOUNDS OF CARBON

The chemistry of the carbon compounds is co-extensive with the wide realm of organic chemistry, in which with very few exceptions all compounds have a covalent constitution. The foundations of the systematization of organic compounds by means of structural formulae, prevailing to the present day, were laid, largely by the efforts of Kekulé, by about 1875. His guiding principle was that the essential four elements, carbon, nitrogen, oxygen, and hydrogen, maintained the constant valencies IV, III, II, and I respectively in all such compounds.

One of the reasons for the enormous proliferation of carbon compounds lies in the particular position of carbon in the assignment of electro-negativities as given in the table on p. 114:

H	C	N	O	Cl	
56	64	70	85	77	(electronegativity, F=100).

Within this range of elements the differences of electronegativity are low enough to ensure that carbon compounds are covalent:

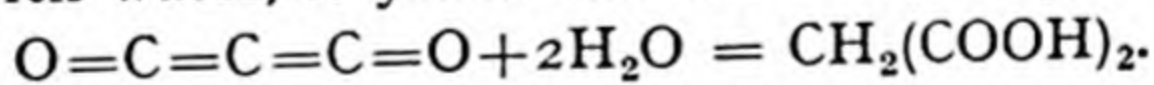


In its metallic compounds, however, carbon is capable of appearing in an anion, as in Be_2C and CaC_2 ; in the latter the anion has the constitution $-\text{C}\equiv\text{C}-$. The nature of *cementite* or iron carbide, Fe_3C , present in iron-carbon alloys, which include steel, is not yet fully agreed.

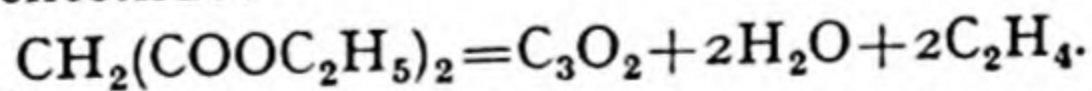
Hydrides. Carbon forms an apparently infinite number of hydrides; they are known as hydrocarbons and are studied in organic chemistry. Several thousand hydrocarbons have already been investigated; among them are *methane*, CH_4 ; *ethane*, C_2H_6 ; *ethylene*, C_2H_4 ; *acetylene*, C_2H_2 ; *benzene*, C_6H_6 ; and *naphthalene*, C_{10}H_8 .

Oxides of Carbon. Several oxides of carbon are known, the principal ones being *carbon suboxide*, C_3O_2 ; *carbon monoxide*, CO ; and *carbon dioxide*, CO_2 .

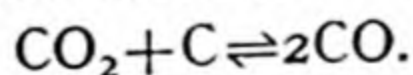
Carbon suboxide, C_3O_2 , is a colourless, poisonous gas with a pungent smell. It boils at 6° and melts at -111° . A mixture of carbon suboxide and oxygen will explode if ignited, forming carbon dioxide. With water, it yields malonic acid, $\text{CH}_2(\text{COOH})_2$:



It is prepared by heating ethyl malonate with a large excess of phosphorus pentoxide:



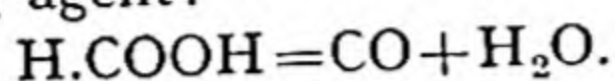
Carbon monoxide, CO . Carbon monoxide is an ingredient of coal-gas, water-gas, and producer-gas. In the laboratory it can be prepared by passing carbon dioxide through red-hot coke:



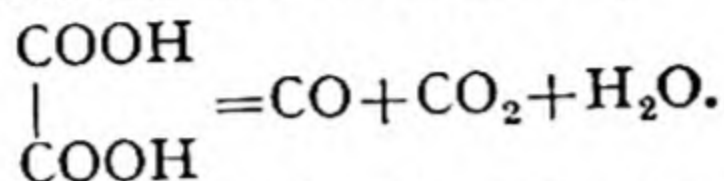
The issuing gases are bubbled through moist soda-lime to remove unchanged carbon dioxide, and the carbon monoxide may then be dried with concentrated sulphuric acid and collected over mercury. If not required dry it can be collected over water.

Alternative methods of preparation are as follows:

1. Formic acid is heated with concentrated sulphuric acid, which acts as a dehydrating agent:

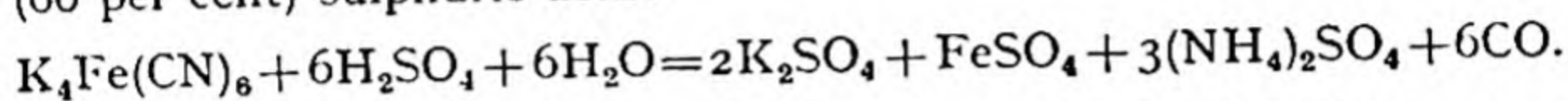


2. Oxalic acid is treated in the same way:



The carbon dioxide is removed with soda-lime.

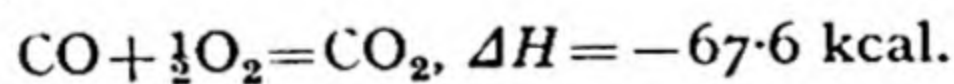
3. Potassium ferrocyanide is heated with moderately concentrated (60 per cent) sulphuric acid:



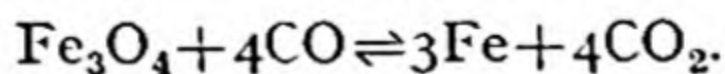
Properties. Carbon monoxide is a colourless, odourless, very poisonous gas; when breathed, it rapidly combines with the oxygen-carrier of the blood (haemoglobin), causing unconsciousness and death. Since it is formed when petrol and coal-gas are burned in confined spaces, care should be taken not to run a motor-car engine in a closed garage, while geysers, gas-stoves, etc., should always be fitted with a flue leading to the exterior. It may be remarked that, owing to the mechanism of its toxic action, viz. combination with haemoglobin, carbon monoxide does not act as a poison upon those living organisms (e.g. plants) which are bloodless.

Carbon monoxide boils at -192° and melts at -207° . It is only slightly soluble in water (35 c.c. per litre at N.T.P.), but dissolves readily in freshly prepared ammoniacal cuprous chloride (p. 317),* forming the compound $\text{CuCl.CO.H}_2\text{O}$, which has been isolated as a white crystalline solid.

Except in the complete absence of moisture, when it is non-inflammable, carbon monoxide will burn in air or oxygen, forming carbon dioxide:



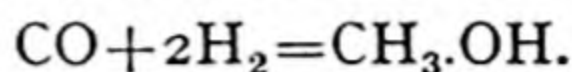
Its affinity for oxygen is great, as shown by the strongly exothermic nature of this combustion; hence it is a powerful reducing agent, especially at high temperatures. In metallurgy, for example, it is commonly employed to reduce metallic oxides to metal:



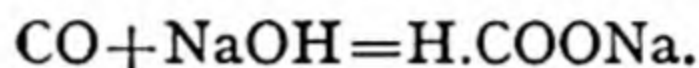
Carbon monoxide combines directly with chlorine in the presence of sunlight, or when the mixed gases are passed over an active carbon catalyst, forming *carbonyl chloride*, or *phosgene*, COCl_2 . If

* And in cuprous chloride dissolved in concentrated hydrochloric acid.

heated with sulphur vapour it yields the gaseous *carbon oxysulphide*, COS; and in the presence of a heated catalyst ($\text{ZnO} + \text{Cr}_2\text{O}_3$) it combines directly with hydrogen to form *methanol* (methyl alcohol):



From the formulae of carbon monoxide and formic acid, and from the fact that formic acid yields carbon monoxide on dehydration, it would be expected that carbon monoxide should act as formic anhydride. This expectation is justified to a certain extent, since although carbon monoxide will not directly combine with water, it reacts with fused caustic soda under pressure, giving *sodium formate*:

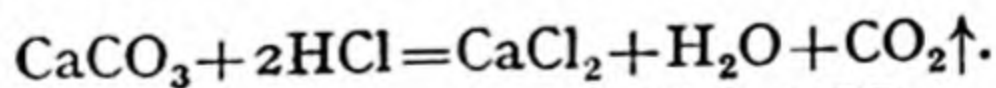


Carbonyls are remarkable compounds of carbon monoxide with metals. Many examples are known, e.g. $\text{Ni}(\text{CO})_4$, nickel carbonyl (p. 601); $\text{Co}_2(\text{CO})_8$; $\text{Fe}(\text{CO})_5$; $\text{Fe}_2(\text{CO})_9$; $\text{Cr}(\text{CO})_6$; and $\text{Mo}(\text{CO})_6$. These are mostly volatile substances, some of which may be prepared by direct combination of carbon monoxide with the metal at slightly elevated temperature and, often, increased pressure.

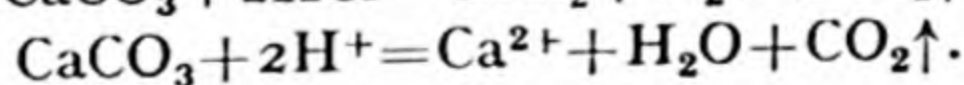
Composition of carbon monoxide. On explosion, a mixture of 2 volumes of carbon monoxide with 1 volume of oxygen yields 2 volumes of carbon dioxide. Assuming carbon dioxide to be CO_2 , it follows from Avogadro's principle that carbon monoxide is CO.

Carbon dioxide, CO_2 . Carbon dioxide is contained in volcanic gases, and frequently issues from crevices in the earth in volcanic regions. It exists in solution in sea-water and other natural waters, and forms 0.03–0.04 per cent by volume of the atmosphere. It is formed during the combustion of carbon and carbonaceous matter, and is a product of the respiration of animals and plants. The proportion of it in the air remains practically constant, however, since much is removed by green plants for use as food, an equivalent volume of oxygen being liberated, while a further 'buffer' is provided by the solution of the gas in sea-water.

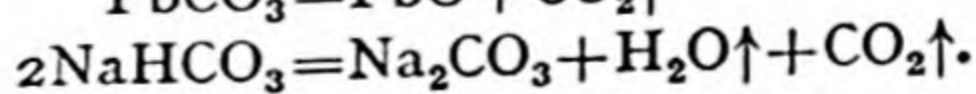
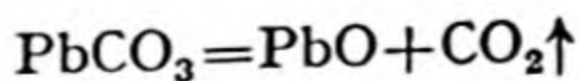
In the laboratory, carbon dioxide is conveniently obtained from a cylinder of the liquid. It can be prepared chemically in many ways, the commonest of which is to add a dilute acid to a carbonate:



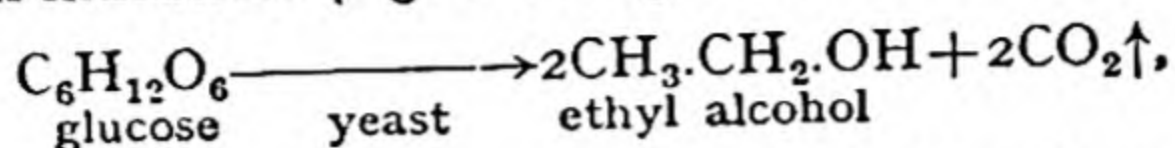
or



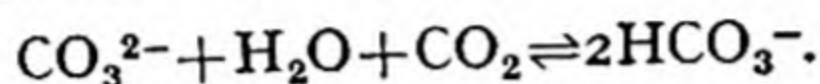
Carbonates (except those of the alkali metals) and bicarbonates yield carbon dioxide on heating. In the case of certain carbonates, e.g. BaCO_3 and CaCO_3 , high temperatures are required to effect the decomposition.



Commercially carbon dioxide is obtained as a by-product in the fermentation industries (e.g. brewing, manufacture of alcohol):

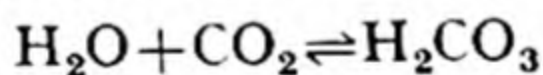


and in the manufacture of quicklime from limestone. It is also prepared by burning coke in a free supply of air. The gaseous mixture of nitrogen and carbon dioxide so formed is passed into cold potassium carbonate solution, when the carbon dioxide is absorbed as bicarbonate. On heating the solution, the bicarbonate is decomposed and the carbon dioxide recovered:



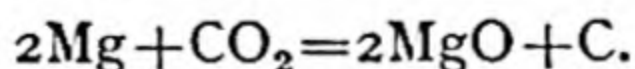
Properties. Carbon dioxide is a colourless gas, with little, if any, smell but a sharp taste ('soda-water'). Its critical temperature is 31° , and it can be liquefied and solidified without difficulty. Solid carbon dioxide is very volatile, its vapour pressure reaching 1 atmosphere at a temperature below the melting-point. Hence at atmospheric pressure solid carbon dioxide sublimates and the liquid cannot stably exist. When liquid carbon dioxide is exposed to the air, part of it vaporizes and the rest solidifies.

Carbon dioxide is moderately soluble in water, 1 c.c. of which dissolves 1.8 c.c. of the gas at 0° . Measurements of the solubility at higher pressures show that Henry's Law (p. 145) is not obeyed under such conditions. The solution contains *carbonic acid*, though the equilibrium shown in the equation

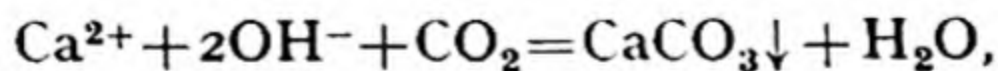


lies very largely to the left. In consequence, carbonic acid behaves as though it were a weak acid (p. 223). It has never been isolated, but its salts, the carbonates and bicarbonates, are well known and important. All bicarbonates are soluble in water, while all carbonates, except those of the alkali metals and ammonium, are insoluble. For descriptions of carbonates and bicarbonates, reference should be made to the chapters on the appropriate metals.

Carbon dioxide will not burn, and is altogether a somewhat unreactive substance. Certain metals, such as sodium, calcium, and magnesium, will burn in it, with liberation of carbon:

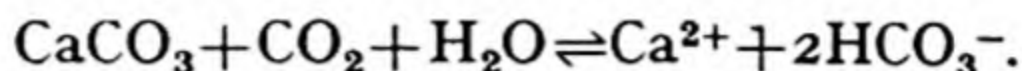


It precipitates calcium and barium carbonates from solutions of the hydroxides:



a reaction used to identify it. Further passage of carbon dioxide

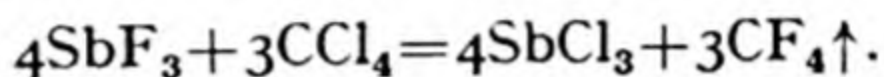
converts these insoluble carbonates into soluble bicarbonates, which are, however, decomposed on boiling the solution:



Uses. As the solid ('dry ice'), carbon dioxide is used as a refrigerant, since it has a high latent heat of sublimation (153 calories per gram as against the 80 calories per gram of latent heat of fusion of ice) and does not melt. Mixed with ether or acetone it forms a freezing-mixture in which temperatures as low as -90° may be reached.

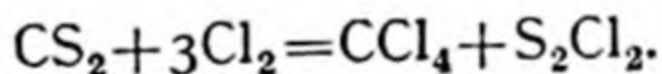
Gaseous carbon dioxide is used in making aerated waters, in the Solvay ammonia-soda process (p. 293), and in fire extinction.

Halides of Carbon. *Carbon tetrafluoride*, CF_4 , is made by the direct union of 'amorphous' carbon and fluorine, or by heating antimony trifluoride, SbF_3 , in carbon tetrachloride vapour:



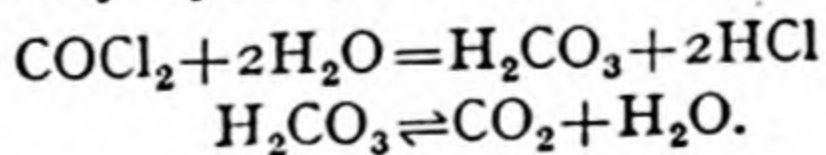
It is a colourless gas, B.P. -130° . Unlike silicon tetrafluoride, it is not hydrolysed by water. Under controlled conditions mixed fluoro-chloro-carbons are obtained, such as CF_2Cl_2 , which is widely used as the working substance in refrigerators, being volatile (B.P. -30°), non-toxic, and non-corrosive.

Carbon tetrachloride, CCl_4 , is prepared by the action of chlorine upon carbon disulphide in the presence of iodine or anhydrous aluminium chloride as catalyst. The other product is sulphur monochloride:

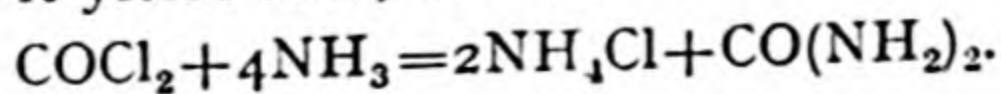


Carbon tetrachloride is a colourless, volatile liquid (B.P. 77°), with a smell resembling that of chloroform, CHCl_3 . It possesses anaesthetic powers, and is a good solvent. Since it is completely non-inflammable and gives a heavy vapour, it is used as a chemical fire-extinguisher. It is a very inert substance, and is not attacked by water.

Carbonyl chloride, or phosgene, COCl_2 , is the acid chloride of carbonic acid. It is made by the direct combination of carbon monoxide and chlorine in sunlight, or in the presence of heated charcoal as a catalyst. Phosgene is a colourless, poisonous gas (B.P. 8°). It is slowly hydrolysed by water:



With ammonia it yields urea, the amide of carbonic acid:



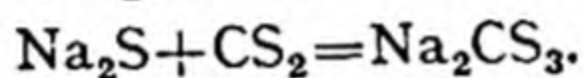
Carbon tetrabromide and *tetra-iodide*, CBr_4 and CI_4 , are crystalline solids. The latter is deep red in colour, and is unstable.

Carbon disulphide, CS_2 , is obtained by heating coke in sulphur vapour in an electric furnace; the action is electrothermic, not electrolytic.

It is a colourless, poisonous, volatile liquid (B.P. 46°), with a sweet and rather pleasant smell when pure. The commercial product contains various other sulphur compounds as impurities, and these give it a nauseous odour; they can be removed by prolonged shaking with mercury and redistillation.

Carbon disulphide is an endothermic substance (ΔH , 27.7 kcal.) and very inflammable. It is a good solvent for sulphur, phosphorus, and fats, and was formerly used in dry-cleaning, a purpose for which it has now been largely replaced by non-inflammable solvents such as trichloroethylene, C_2HCl_3 .

It dissolves in concentrated sodium sulphide solution, forming *sodium thiocarbonate*, analogous to sodium carbonate:



Nitrogenous compounds of carbon, e.g. *cyanogen*, C_2N_2 ; *hydrogen cyanide*, HCN ; and *potassium cyanide* and *cyanate*, KCN and KOCN , are studied in organic chemistry.

15321

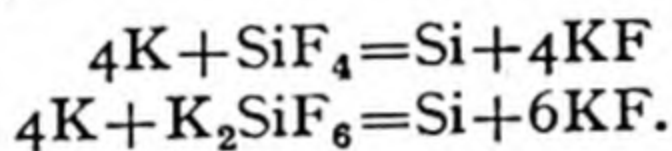
SILICON, Si

Atomic number: 14. *Atomic weight:* 28.09. *Specific gravity:* 2.4.
Melting-point: 1,420°. *Boiling-point:* 2,350°.

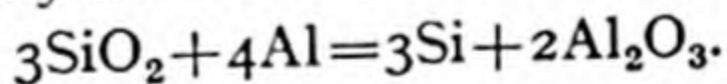
History. In 1660, TACHENIUS showed that *silicon dioxide*, or *silica*, SiO_2 , possesses acidic properties. LAVOISIER (1787) assumed silica to be the oxide of an unknown element, and in 1809-11 GAY-LUSSAC and THENARD prepared crude silicon by heating potassium in the gaseous compound *silicon fluoride*, SiF_4 . DAVY showed silicon to be a non-metal, and pointed out its resemblance to carbon.

Occurrence. Silicon does not occur free in nature, but its compounds silica and the silicates are so abundant (as sand, flint, clay, slate, etc.) that silicon forms about a quarter of the earth's crust, by weight.

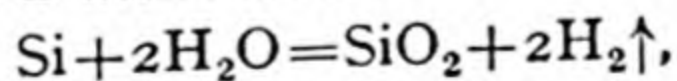
Preparation. In the amorphous (perhaps microcrystalline) form, silicon can be obtained by heating sodium or potassium in silicon tetrafluoride, or by fusing either of these metals with sodium or potassium fluosilicate:



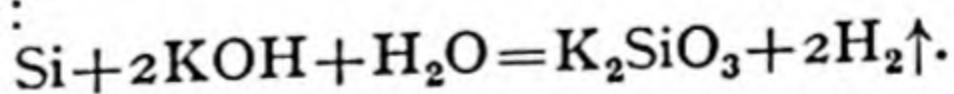
A crystalline variety (probably containing alloyed aluminium; see boron, p. 372) may be prepared by the GOLDSCHMIDT or aluminothermic method (p. 380); silica is mixed with aluminium powder—and in this case with flowers of sulphur as well, in order to obtain greater heat—and the mixture is ignited by a piece of burning magnesium ribbon. The action is very energetic, and yields a residue of silicon, aluminium oxide, aluminium sulphide, and unchanged aluminium. This is washed with dilute hydrochloric acid and then with hydrofluoric acid, when the silicon is left:



Properties. Amorphous silicon is a brown powder which burns when strongly heated in air or oxygen, giving silica, SiO_2 . It decomposes steam at a white heat:



and is readily dissolved by hot concentrated caustic alkali solution, forming *silicates*:



It dissolves in certain fused metals, forming true solutions; with others it combines to give *silicides*, e.g. Mn_2Si , Mg_2Si , FeSi . When heated in chlorine, it burns, forming *silicon tetrachloride*, SiCl_4 .

Crystalline silicon has a metallic appearance, but has a low electrical conductivity.

Industrially silicon is used in making acid-resisting silicon steels, which may contain as much as 50 per cent Si.

COMPOUNDS OF SILICON.

Silicon hydrides. When solutions of silicon tetrachloride and of lithium aluminium hydride in ether are mixed *monosilane*, SiH_4 , is produced in almost quantitative yield:

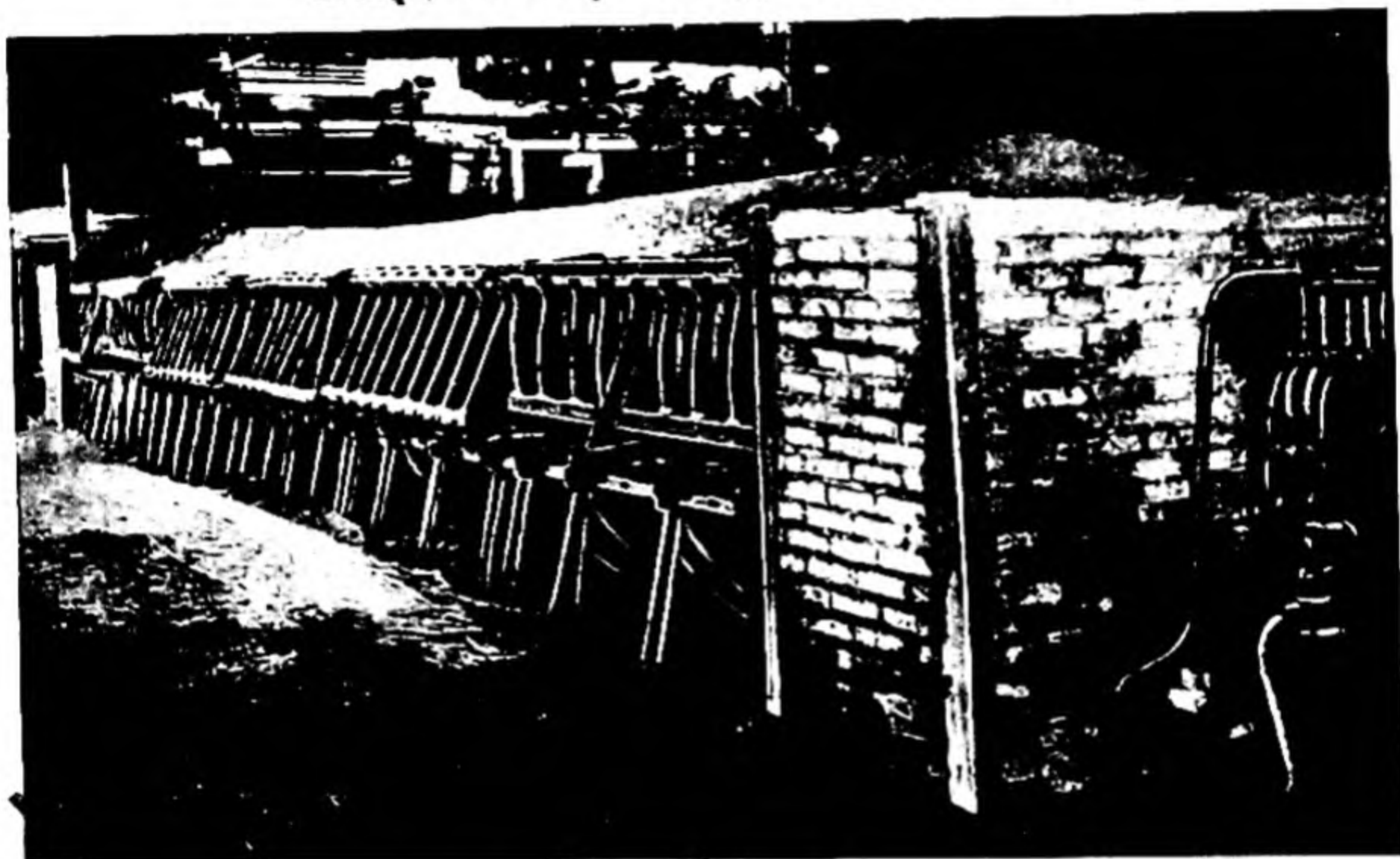
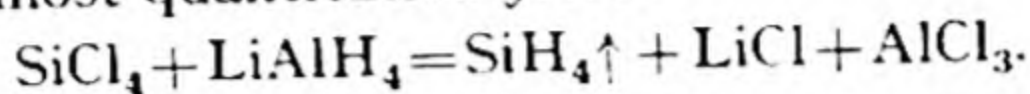
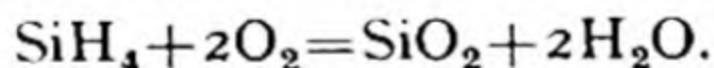


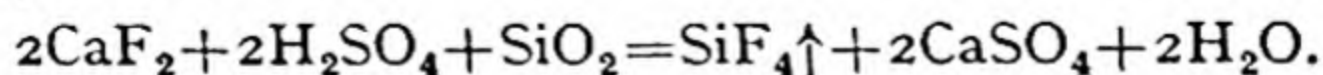
FIG. 77. CARBORUNDUM FURNACE

Monosilane is a colourless gas (B.P. -112°) with a peculiar smell. It is spontaneously inflammable in air, burning to silica and steam:



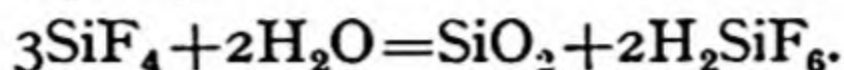
Other hydrides, such as *disilane*, Si_2H_6 , and *trisilane*, Si_3H_8 , have been prepared. In structure they resemble the corresponding hydrocarbons.

Silicon tetrafluoride, SiF_4 , is obtained by heating a mixture of powdered calcium fluoride (fluorspar) and fine sand with concentrated sulphuric acid:

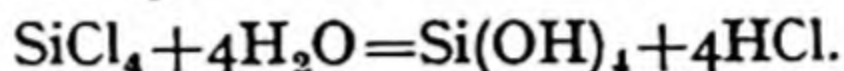


It is a colourless, non-inflammable gas with a pungent smell. It must be collected over dry mercury, since it is immediately

hydrolysed by water into gelatinous silica and *fluosilicic acid* (*silicofluoric acid*), H_2SiF_6 :



Silicon tetrachloride, SiCl_4 , is a colourless liquid formed when silicon, or a mixture of silica and carbon, is heated in chlorine. It is rapidly decomposed by water:



If silicon is heated in hydrogen chloride, the colourless liquid *silico-chloroform*, SiHCl_3 , is obtained:

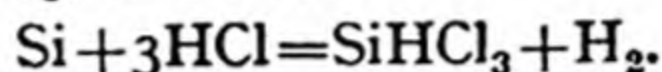
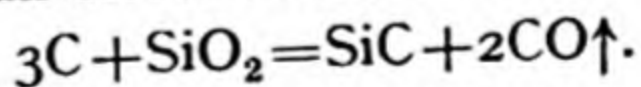


FIG. 78. CRYSTALS OF SILICON CARBIDE

Like the tetrachloride, this is hydrolysed by water, and resembles chloroform only in structure.

Silicon carbide, SiC , a popular commercial brand of which is known under the trade name of *carborundum*, is a very hard substance made by heating a mixture of sand, coke, sawdust, and a little common salt in an electric resistance furnace:



It is used as an abrasive, in powder or as a grindstone, and since it withstands high temperatures and is chemically unreactive it is employed for making crucibles, furnace-linings, etc.

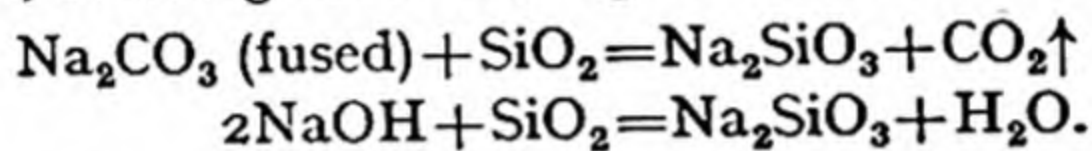
Silicon monoxide, SiO , obtained as a vapour by heating silica with silicon in the correct proportions to a high temperature, decomposes to the original mixture on cooling.

Silicon dioxide, silica, SiO_2 , occurs naturally in the amorphous

form as *flint*, *opal*, and *kieselguhr*,* and in three crystalline forms, viz. *quartz*, *tridymite*, and *cristobalite*. Pure, transparent, colourless quartz is called *rock-crystal*; coloured by traces of manganese and iron it forms *amethyst*; while in a state of more or less fine division it is *sand*.

When quartz is heated to 870° , it changes its crystalline structure and is converted into tridymite, and this in turn becomes cristobalite at $1,470^{\circ}$. At $1,710^{\circ}$ cristobalite melts to a clear liquid, which on cooling sets to a transparent, glassy solid, 'silica glass.' Silica glass finds many applications, since (i) it has a very small coefficient of expansion, so that articles made of it do not crack when suddenly heated or cooled; (ii) its refractive index is only slightly lower than that of glass, and it is transparent to ultra-violet and infra-red rays, so that it is useful for optical apparatus and ultra-violet mercury-lamps; (iii) it is very resistant to many chemical reagents; and (iv) it is much less soluble in water than ordinary glass.

Silica is soluble in fused alkalis, and less easily in hot concentrated alkali solution, forming silicates, e.g. sodium silicate, Na_2SiO_3 :



A concentrated syrupy solution of a variety of sodium silicate is sold, under the name of *water-glass*, for preserving eggs and as an adhesive, e.g. in making cardboard boxes.

Silicic acid. A gelatinous, colloidal, white precipitate is formed when silicon tetrachloride is hydrolysed by water. A precipitate similar in appearance is formed when concentrated hydrochloric acid is added to a concentrated solution of sodium silicate. The composition of these precipitates is indefinite, and it is impossible to write simple chemical formulae to represent them.

If a dilute solution of sodium silicate is added to dilute hydrochloric acid, a colloidal solution of silicic acid is obtained, from which the sodium chloride may be removed by dialysis (p. 257). Silicic acid behaves as a very weak acid.

Glass. The Roman writer PLINY says that glass was discovered by Phoenician traders on the beach at the foot of Mount Carmel in Palestine. 'The shore does not exceed half a mile in extent, and yet, for long ages, it was the only source of sand for making glass. The story is that merchants put in there with a cargo of crude soda, and when, scattered over the beach, they were preparing a meal and could find no stones of the right height to prop their pots, they supported them on lumps of soda which they had fetched from the

* This consists of the siliceous part of the cell-walls of the minute algae known as *Bacillariales* or *Diatoms*.

ship. When these were melted by the heat and mingled with the sand, transparent streams of a strange liquid were seen to flow, and thus glass was discovered.*

There is, however, every reason to suppose that this story is untrue, for glass was known to the Egyptians in very much more remote times. Archaeologists, indeed, hold that glass was an

Egyptian invention, and it is at least certain that glass manufacture was practised on a very large scale under the Pharaohs. Nevertheless, the Phoenicians are not left without credit, for it is widely believed that the art of glass-blowing, as distinct from the older method of glass-moulding, was invented by them in their city of Sidon about the beginning of the Christian era. The skill of the ancient glass-workers is admirably exemplified in the Portland Vase (British Museum), which dates from the first century B.C. Unfortunately it was smashed by a lunatic in 1845, but it has been so deftly reassembled that much of its pristine beauty remains.



British Museum

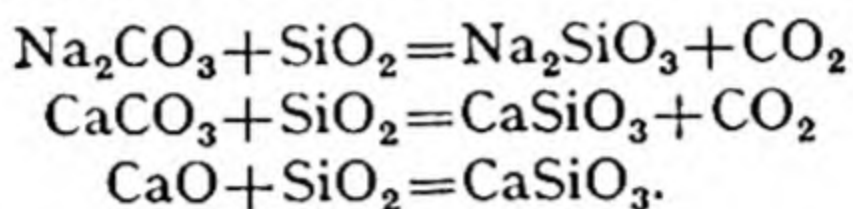
FIG. 79. THE PORTLAND VASE

Glass is a homogeneous mixture of two or more silicates, the most common of which are the silicates of sodium, calcium, potassium, and lead. Though it appears to be solid, it has sometimes been regarded as an under-cooled liquid, since it has no definite melting-point or crystalline structure; on heating, it gradually becomes softer and more mobile, but there is no sharp change from 'solidity' to 'fluidity.' When, however, glass is stored for a considerable period, or if it is heated to the point at which it becomes definitely soft, some of its ingredients may crystallize. This process is known

* K. Bailey, *The Elder Pliny's Chapters on Chemical Subjects*, vol. ii (London, E. Arnold & Co., 1932).

as *devitrification*, since the glass then loses its transparency and readily falls to pieces on heating.

Common glass is made by melting together sand (SiO_2), soda-ash (Na_2CO_3), and quicklime (CaO) or limestone (CaCO_3); in practice a little charcoal is usually added as well, as this gives a better product. To make the various constituents melt together more easily and more fully, a certain amount of 'cullet,' i.e. broken scrap glass, is mixed with them. The product after fusion consists of a mixture of sodium silicate and calcium silicate with an excess of silica, and is the common soda-glass such as is used for windows and glass-tubing:



A harder type of glass is made by using potassium carbonate instead of sodium carbonate, while 'crystal glass,' from which cut-glass jugs, tumblers, vases, etc., are made, is prepared by melting together sand, red lead (Pb_3O_4), potassium carbonate (K_2CO_3), and cullet. 'Pyrex' glass contains borates as well as various silicates: glass used for optical purposes frequently contains lead silicate and zinc silicate, or, in CROOKES'S glass, compounds of neodymium and praseodymium which cut off the ultra-violet rays; while bottle glass is a mixture of the silicates of sodium, calcium, aluminium, magnesium, and iron. In making white glass, the best white sand has to be used, and iron must be absent or the glass will be greenish. Since the removal of all iron is frequently a matter of difficulty, a trace of manganese dioxide ('glassmaker's soap') is added to the ingredients; this neutralizes the green colour, as has been known for some two thousand years.

Coloured glass is made by adding to the main materials, before fusion, small quantities of other substances, the proportions being varied according to the depth of the colour required. The following table shows the substances used to give glass some of the more popular colours:

Colour	Substance added
Blue	Cobalt oxide, CoO ; cupric oxide, CuO
Red	Gold chloride, AuCl_3 ; cuprous oxide, Cu_2O
Violet	Manganese dioxide, MnO_2
Green	Chromium sesquioxide, Cr_2O_3
Yellow	Certain antimony compounds; cadmium sulphide, CdS
Opal	Bone ash, calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$

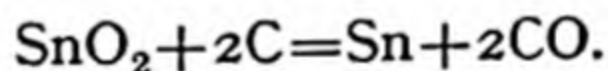
TIN, Sn

Atomic number: 50. *Atomic weight:* 118.7. *Specific gravity:* 7.2.
Melting-point: 232°. *Boiling-point:* 2,360°.

History. The Cassiterides, or Tin Islands, visited by Phoenician adventurers may have been Cornwall and St. Michael's Mount. Tin was certainly mined in Cornwall in very remote times, and DIODORUS SICULUS says that, after casting it in ingots, the Britons brought it to an island which was joined to the mainland at low tide. Thence it was shipped to Gaul, and carried on horses for a thirty days' journey to the mouth of the Rhône, *en route* for Rome. Tin was also known to the Egyptians and other ancient nations. The symbol Sn is derived from a Latin name of the metal, *stagnum*, or *stannum*, itself possibly derived from the Phoenician name, *stan*.

Occurrence. Though the occurrence of specimens of native tin has been reported from time to time, practically the sole source of the metal is its dioxide ore *cassiterite* or *tinstone*, SnO_2 . Small quantities of this mineral occur in many parts of the world, but the principal deposits are in the Malay Peninsula, Indonesia, Bolivia, and Mexico.

Extraction. The ore is powdered, and washed in a current of water; this carries off the less dense particles of earth, sand, etc., leaving behind the denser ore particles (specific gravity about 7). The concentrated ore is placed in a rotating furnace, and roasted in a current of air, to remove arsenic and sulphur, again washed, and finally reduced to metal by heating with anthracite in a reverberatory furnace:



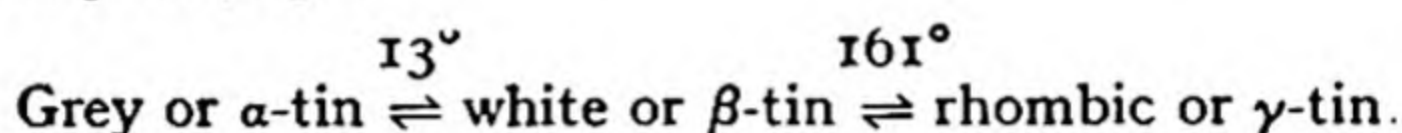
The molten tin is run off from the bottom of the furnace on to a sloping hearth, where the dross—which has a higher melting-point—solidifies while the still liquid metal flows on into moulds.

Tin fetches a high price, so that the process of de-tinning old tin-plate (p. 414) articles is commercially profitable. In one method, the articles are treated with chlorine under pressure, when volatile stannic chloride (SnCl_4) is formed. This is either used directly for 'weighting' silk stockings, or hydrolysed by water to hydrated stannic oxide, which can be dried and reduced with anthracite, as above. The residual scrap iron is used for making steel.

Properties. Tin is a white metal capable of receiving a very high polish. It melts at 232°, boils at 2,360°, and has a specific gravity of 7.2–7.3. It is ductile and malleable, and can be pressed or rolled into tin-foil or 'silver paper.' On bending, a bar of tin may be heard to emit a faint crackling noise, the so-called 'cry of tin'; this has been attributed to friction between the metallic crystals.

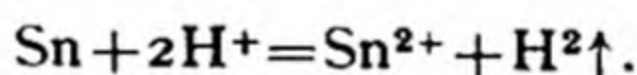
Common tin, known as white tin or β -tin, is only one of three allotropic modifications. If it is heated to 161° , it changes to γ -tin, which consists of rhombic crystals as opposed to the tetragonal crystals of β -tin. If, on the other hand, β -tin is cooled below 13° , it slowly turns to a voluminous grey powder of α -tin; the change occurs most quickly at about -50° , and is catalysed by solutions of electrolytes. Inoculation of white tin with grey tin also greatly accelerates the change, and since the metal appears to be suffering from some infectious disease the process of transformation has been called 'tin plague.' Its destruction of tin objects preserved in museums in cold countries is a minor disaster.

When grey tin is heated, it is reconverted into white tin at the transition point, 13° :



Tin is quite stable in air at room temperature, even in the presence of water. When heated, it melts and gradually becomes covered with a film of *stannic oxide*, SnO_2 (or perhaps a mixture of this with finely divided tin). At a high temperature tin can be made to burn in air, and to liberate hydrogen from steam.

It dissolves slowly in dilute hydrochloric acid and dilute sulphuric acid with liberation of hydrogen and formation of *stannous chloride*, SnCl_2 , and *stannous sulphate*, SnSO_4 , respectively:



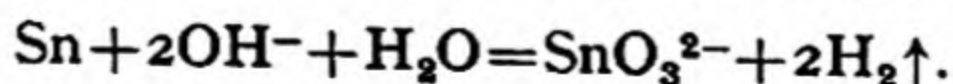
Concentrated hydrochloric acid dissolves it readily, in the same way; while hot concentrated sulphuric acid attacks it vigorously, giving *stannic sulphate*, $\text{Sn}(\text{SO}_4)_2$, sulphur dioxide, and sulphur. The reaction cannot be satisfactorily expressed by a single equation.

Dilute nitric acid dissolves tin, to form *stannous nitrate*, $\text{Sn}(\text{NO}_3)_2$, and ammonium nitrate:



Since some stannic ions are found in the resulting solution, it is clear that this equation is no more than approximate. The concentrated nitric acid of the reagent shelves attacks tin furiously, yielding a white insoluble powder known as *metastannic acid*; this is a hydrated stannic oxide of the approximate composition $\text{H}_2\text{Sn}_5\text{O}_{11}$.

Tin dissolves in hot concentrated solutions of caustic alkalis, with formation of *stannates* and liberation of hydrogen:

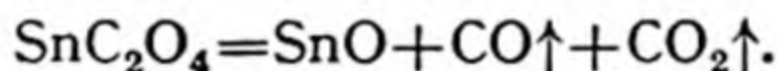


Uses. The chief use of tin is in the manufacture of tin-plate, i.e. sheet-iron covered with a thin coating of tin. The iron is cleaned by 'pickling' in dilute sulphuric acid and is then dipped into melted tin. Tin-plate is widely employed in the form of cans and 'tins' for the storage of food, since tin is not attacked by organic acids, etc. Block (i.e. solid) tin is used in stills and condensers for making pure distilled water. Tin-foil is used as a wrapping-material. Tin is an ingredient of many important alloys, e.g. *pewter*, *phosphor-bronze* (for these see p. 420), *bronze* (p. 314), *bell-metal* (Cu, 80 per cent; Sn, 20 per cent), *speculum metal* (Cu, 67; Sn, 33 per cent), *babbitt* (Sn, 90; Sb, 7; Cu, 3 per cent), *Britannia metal* (Sn, 85; Sb, 9; Zn, 2; Cu, 2; Bi, 2 per cent), and *aluminium solder* (Sn, 86; Zn, 9; Al, 5 per cent).

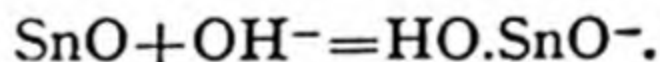
COMPOUNDS OF TIN: STANNOUS COMPOUNDS

Tin forms two series of compounds, the *stannous* in which it is bivalent, and the *stannic* in which it is quadrivalent. Both the stannous ion, Sn^{2+} , and the stannic ion, Sn^{4+} , are colourless; and the latter is usually (if not always) hydrated, $[\text{Sn} \cdot 6\text{H}_2\text{O}]^{4+}$. Stannous salts are good reducing agents, since the quadrivalent state of the metal is much more stable than the bivalent.

Stannous oxide, SnO , like ferrous oxide (p. 591), can be made by heating the oxalate in the absence of air:

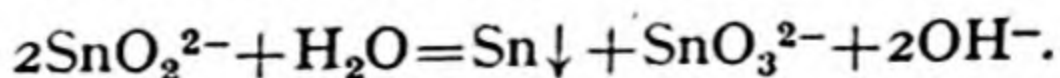


It can also be obtained by gently heating the hydroxide under the same conditions. It is a greyish-green solid, which spontaneously smoulders and oxidizes in the air, forming stannic oxide. With a dilute acid it yields a stannous salt, but it also dissolves in aqueous alkalis to form *stannites*:

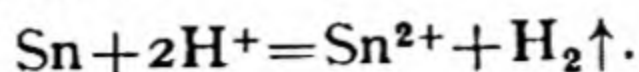


These resemble the plumbites (p. 421), and are readily oxidized to stannates.

Stannous hydroxide, $\text{Sn}(\text{OH})_2$, has probably not yet been prepared pure. The white precipitate obtained when caustic soda solution is added to a solution of a stannous salt was shown by BURY and PARTINGTON to be a hydrated stannous oxide, $3\text{SnO} \cdot 2\text{H}_2\text{O}$. Like stannous oxide itself, this is amphoteric, dissolving both in dilute acids and in alkalis. The solution in caustic soda contains sodium stannite; on standing, it gives a precipitate of stannous oxide, and if boiled yields tin and a solution of sodium stannate:

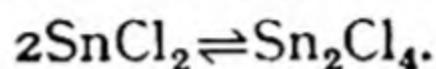


Stannous chloride, SnCl_2 , is prepared by dissolving tin in concentrated hydrochloric acid:



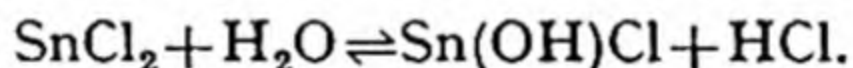
It crystallizes from solution as the colourless *dihydrate*, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$. To prepare the anhydrous salt the metal is heated in a current of hydrogen chloride, since the dihydrate is hydrolysed if heated in the air; hydrolysis can, however, be prevented if the salt is heated in hydrogen chloride.

Anhydrous stannous chloride (M.P. 247° , B.P. 603°) is a glass-like solid, the vapour of which is slightly associated:



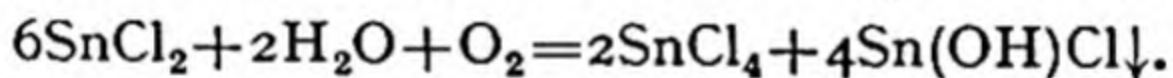
It is readily soluble in organic solvents such as ether and acetone, and is therefore regarded as covalent.

The hydrated salt is used as a mordant in the dye industry, under the name of *tin salt*. It dissolves to a clear solution in a small quantity of water, but on dilution hydrolysis occurs and a white basic chloride, *stannous oxychloride*, is precipitated:

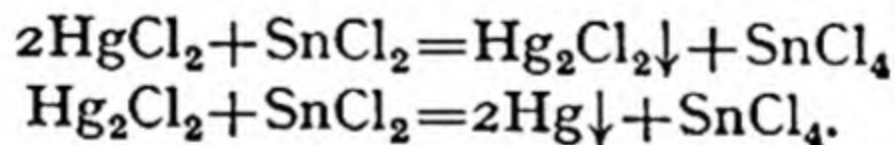


Addition of hydrochloric acid to the original solution prevents the formation of the oxychloride, partly by mass-action effect, and partly because a complex anion, SnCl_4^{2-} is formed.

Stannous chloride is a vigorous reducing agent, its solution becoming turbid through oxidation even on exposure to air:

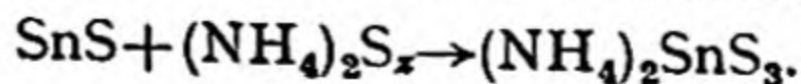


Stannous chloride will reduce mercuric chloride to mercurous chloride, and the latter still further, to metallic mercury:

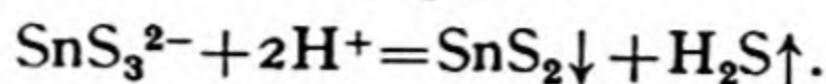


It will also reduce chromates to chromium salts, and ferric salts to ferrous salts. It is, however, itself reduced to metallic tin by zinc; thus if zinc is added to a solution of stannous chloride, crystals of tin are deposited, often in an arborescent form ('tin tree').

Stannous sulphide, SnS , can be prepared synthetically, but is most familiar as the brown precipitate obtained by passing hydrogen sulphide into a solution of a stannous salt, as in Group II of the qualitative analysis tables. It is soluble in concentrated hydrochloric acid (distinction from arsenic), and also dissolves in *yellow ammonium sulphide* to form ammonium thiostannate:



On addition of acid to the solution, a precipitate is obtained; this is stannic sulphide, not stannous sulphide:

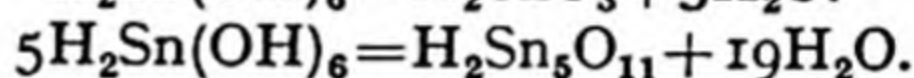
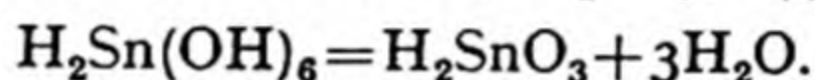


COMPOUNDS OF TIN: STANNIC COMPOUNDS

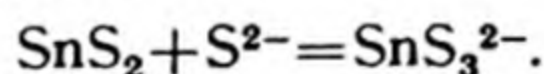
Stannic hydride, SnH_4 , is an unstable gas.

Stannic oxide, SnO_2 , can be prepared by acting upon tin with ordinary concentrated nitric acid and igniting the residue of stannic acid (p. 413). It is an unreactive substance of slightly amphoteric character. On fusion with caustic soda it yields sodium stannate, Na_2SnO_3 . Industrially it is used in making white opaque glass and enamels.

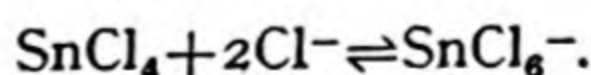
Stannic Acids. If a solution of sodium stannate is acidified, a white precipitate of α -stannic acid, H_2SnO_3 , is formed. *Metastannic acid*, or β -stannic acid, is the white solid obtained by the action of concentrated nitric acid on tin. Both α - and β -stannic acids are very weak acids. They may be regarded as dehydration products of the hypothetical *orthostannic acid*, $\text{H}_2\text{Sn}(\text{OH})_6$.



Stannic sulphide, SnS_2 , is a bright yellow pigment ('mosaic gold') made by heating a mixture of tin, sulphur, and ammonium chloride. In qualitative analysis, it appears as a yellowish precipitate in Group II. It dissolves readily in concentrated hydrochloric acid, and will also dissolve, as the thiostannate, in either colourless or yellow ammonium sulphide:



Stannic chloride, SnCl_4 , was discovered by LIBAVIUS (c. 1540–1616) and was therefore formerly known as *spiritus fumans Libavii*, 'Libavius's fuming spirit.' It is a colourless liquid (M.P. -33° , B.P. 114°) made by heating tin in a current of chlorine, or by passing carbon tetrachloride vapour over heated stannic oxide. In moist air it fumes, owing to hydrolysis, and—like stannous chloride—it dissolves in a *small* quantity of water. Dilution causes hydrolysis, with precipitation of hydrated stannic oxide. Addition of hydrochloric acid reduces the hydrolysis and also gives rise to complex ions:



SnCl_6^{2-} is the anion of *chlorostannic acid*, the ammonium salt of which (ammonium chlorostannate, $(\text{NH}_4)_2\text{SnCl}_6$) is used in dyeing as a mordant under the name of 'pink salt.' 'Butter of tin,' also used in dyeing, is stannic chloride pentahydrate, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$.

From its general characteristics, stannic chloride appears to be covalent, but the hydrate is most probably ionic.

Tests for Tin.

1. Charcoal block: white malleable beads, yellow (hot) or white (cold) incrustation.
2. *Stannous* salts give with
 - (a) sodium hydroxide solution: white precipitate of hydrated stannous oxide, $3\text{SnO} \cdot 2\text{H}_2\text{O}$, soluble in excess;
 - (b) hydrogen sulphide: brown precipitate of stannous sulphide, SnS , soluble in concentrated hydrochloric acid and in *yellow* ammonium sulphide;
 - (c) mercuric chloride: white precipitate of mercurous chloride, Hg_2Cl_2 , later reduced to metallic mercury.
3. *Traces* of a stannous salt may be detected by the intense blue colour they give with ammonium phosphomolybdate; this must be washed free from nitric acid if prepared as in the phosphate test (p. 474).
4. *Stannic* salts give with
 - (a) sodium hydroxide solution: white precipitate of hydrated stannic oxide, soluble in excess;
 - (b) hydrogen sulphide: yellow precipitate of stannic sulphide, SnS_2 , soluble in yellow or *colourless* ammonium sulphide;
 - (c) mercuric chloride solution: no precipitate (distinction from stannous salts).

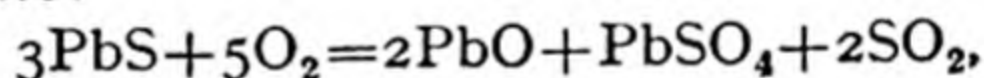
LEAD, Pb

Atomic number: 82. *Atomic weight:* 207.2. *Specific gravity:* 11.34.
Melting-point: 327°. *Boiling-point:* 1,755°.

History. Lead has been known from very early times, and was called *plumbum nigrum* by the Romans to distinguish it from *plumbum candidum*, tin. The lead mines of Britain were worked as early as the first century A.D., and some of the metal was desilverized, for a pig of Romano-British lead has been discovered marked EX. ARG., i.e. 'silver extracted.' Even as late as the Middle Ages, lead-mining was an important English industry, and several curious laws and regulations were made concerning it. Any miner found whistling in the mine was flogged, for it was believed that whistling frightened the lead ore away. Among the alchemists, lead was known as Saturn and astrologically connected with the planet.

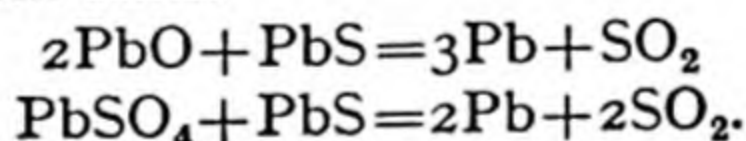
Occurrence. The principal ore of lead is *galena*, PbS. Other lead minerals are *cerussite*, PbCO₃; *anglesite*, PbSO₄; and *crocoisite*, PbCrO₄. The chief deposits of galena (which is usually argentiferous; see p. 322) occur in the United States, Mexico, Spain, Germany, and Australia.

Extraction. Galena is roasted in a regulated supply of air. Under these conditions some of the lead sulphide is oxidized to lead oxide and lead sulphate:



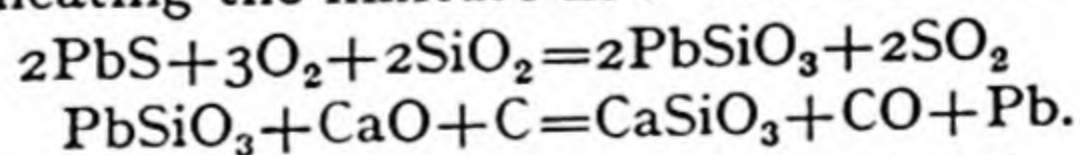
and some is left unchanged.

At this stage the air supply is interrupted and the temperature raised. The unaltered galena now reacts with the lead oxide and lead sulphate to form lead:



The sulphur dioxide is diverted to a sulphuric acid plant, and the molten lead is run off and cast into ingots.

In another process, galena ore contaminated with silica (a frequent phenomenon) is successfully treated by mixing it with lime and coke and strongly heating the mixture in a blast furnace:



The calcium silicate forms a slag immiscible with the molten lead.

The crude lead contains many impurities, commonly arsenic, antimony, bismuth, zinc, and silver. Partial purification is effected by melting the metal in a furnace, when most of the impurities (except bismuth and silver) and a little of the lead are oxidized, and rise to the surface as a scum. This is removed, and desilverization

of the lead is then carried out by one of the processes described on p. 323. Further purification, if necessary, may be effected electrolytically, using the impure lead as anode, a sheet of pure lead as cathode, and an electrolyte of lead fluosilicate, PbSiF_6 .

Properties. Lead is a soft greyish-white metal, with a pronounced blue tinge when impure; freshly cut surfaces are lustrous, but superficial tarnishing soon occurs in the air. The specific gravity of lead is 11.34; it melts at 327° and boils at $1,755^\circ$. It is ductile and malleable, and, when hot, may be forced through a hole; this process is called 'squirting.' Lead piping is made by squirting, while sheet lead is made by passing a bar of lead between heavy rollers.

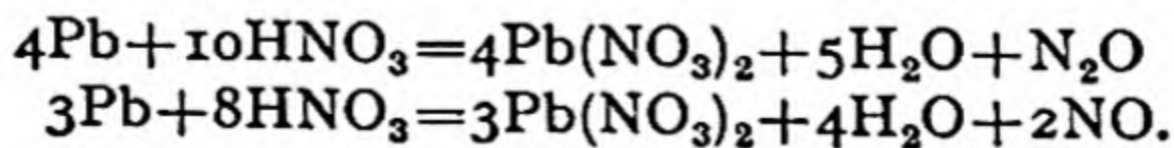
On exposure to air, lead is rapidly covered with a film of oxide, hydroxide, and carbonate, which protects it from further attack; the finely divided metal is, however, pyrophoric—that is, it takes fire spontaneously in the air, especially when slightly heated. Lead 'sponge,' precipitated by zinc or magnesium from aqueous solutions of lead salts, reduces nitrates (e.g. barium nitrate) to nitrites, at the boiling temperature. When molten lead is heated and stirred in air, it is gradually converted into *lead monoxide*, PbO ; at a higher temperature this in turn is oxidized to *triplumbic tetroxide*, or 'red lead,' Pb_3O_4 .

Lead is not attacked by pure water free from dissolved oxygen or air. Ordinary soft water, however, from which the dissolved air has not been boiled out, attacks lead fairly rapidly, *plumbous hydroxide*, $\text{Pb}(\text{OH})_2$, passing into solution. Since lead compounds act as cumulative poisons, remaining in the body and not passing out with the excreta, continued drinking of soft water which has passed through lead pipes is liable to cause lead-poisoning or 'plumbism.' Hard water attacks lead equally, if not more, quickly, but the action soon stops owing to the deposition of a protective coherent film of lead carbonate or sulphate.

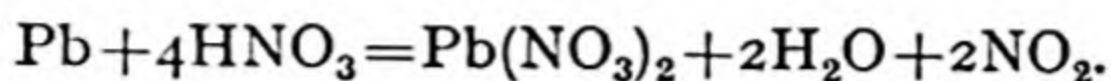
Lead combines directly with chlorine, forming *plumbous chloride*, PbCl_2 , and with sulphur, forming *plumbous sulphide*, PbS . It is not easily attacked by non-oxidizing acids (see electrochemical series, p. 244), though hot concentrated hydrochloric acid slowly converts it into plumbous chloride with evolution of hydrogen. Hot concentrated sulphuric acid dissolves it, sulphur dioxide being given off:



It also dissolves readily in dilute nitric acid, yielding nitric oxide, nitrogen dioxide, nitrous oxide, ammonium nitrate, etc., according to the conditions, e.g.:



With concentrated nitric acid, the chief gaseous product is nitrogen dioxide:



In the presence of air, lead is rapidly attacked even by such weak acids as acetic and carbonic (see lead carbonate).

Uses. Both lead and lead alloys find extensive and varied applications. Sheet lead, made either by casting or by passing an ingot of the metal through rollers, is used for roofing and for lining tea-chests, etc. The chambers of old-fashioned sulphuric acid works were lined with lead, and lead sheets, or 'mattresses,' are often included in the foundations of tall buildings, to lessen vibration. In leaded windows, in plumb-bobs, in X-ray shields, in the sheathing of electric cables, and in weighting the keels of yachts, leads finds a further selection of its manifold uses. It is also indispensable as piping, and as the principal material of which accumulator plates are made.

Some of the principal alloys of lead are shown in the following table:

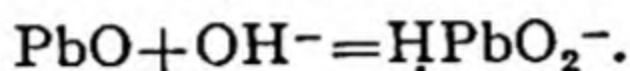
<i>Alloy</i>	<i>Composition (approximate or usual) Per cent by weight</i>
Soft solder	Pb 58, Sn 40, Sb 2
Plumbers' solder	Pb 69, Sn 30, Sb 1
Linotype metal	Pb 84, Sn 4, Sb 12
Stereotype metal	Pb 76, Sn 8, Sb 16
White metal, for bearings	Pb 88, Sb 12
Former G.W.R. white metal driving-box bearings	Pb 28.4, Sn 59.5, Sb 9.9, Ni 2.5, Cu 2.5
Phosphor-bronze	Pb 10, Sn 10, Cu 79, P 1
Rose's fusible alloy	Pb 25, Sn 25, Bi 50
Lipowitz's fusible alloy	Pb 27, Sn 13, Bi, 50, Cd 10
Pewter	Pb 2, Sn 89, Sb 7, Cu 2
Small shot alloy	Pb 99.95, As 0.05
Rifle bullet alloy	Pb 98, Sb 2
Shrapnel alloy	Pb 87, Sb 13
Accumulator plates	Pb 92, Sb 8

Lead forms two series of compounds, the *plumbous* and the *plumbic*, in which it is bivalent and quadrivalent respectively. The ion Pb^{2+} occurs in some plumbous salts (e.g. nitrate and sulphate), but plumbic compounds are nearly all covalent in constitution, with the possible exception of the dioxide, PbO_2 .

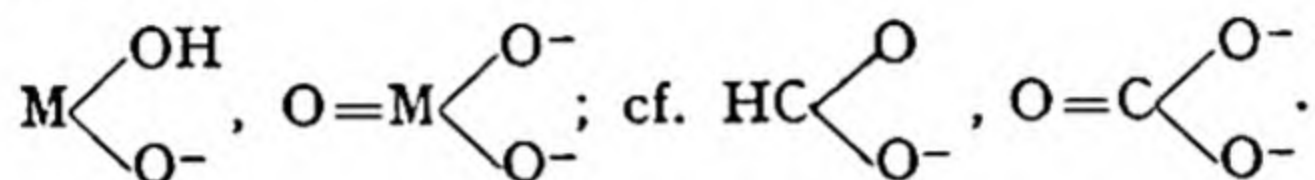
COMPOUNDS OF LEAD: PLUMBOUS COMPOUNDS

Lead monoxide, PbO , is known as *massicot* when in the form of an orange-yellow powder. When fused and allowed to solidify, it crystallizes as a reddish solid, *litharge*, of the same composition. It is obtained by melting lead and blowing a current of air over the heated, molten metal; commercially it is used in glazing pottery, in making flint glass, and in the manufacture of other lead compounds.

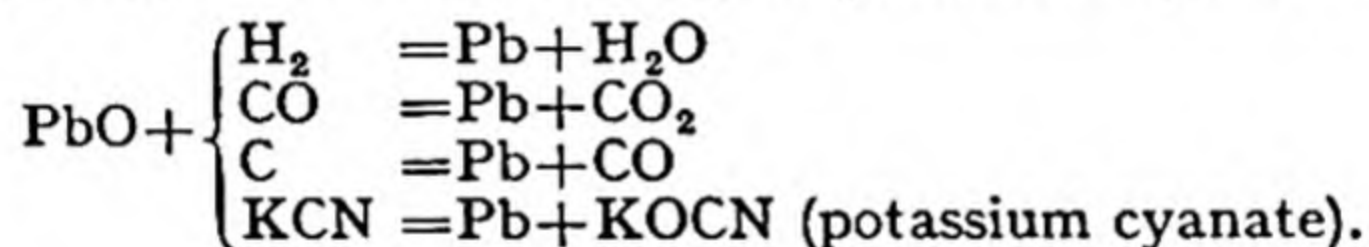
Lead monoxide dissolves in acids to form lead salts, and in hot caustic alkali solution to form *plumbites*:



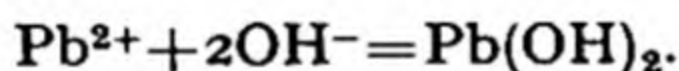
The following structures may be provisionally assigned to oxyanions of lead and tin ($\text{M} = \text{Pb}$ or Sn), but they await experimental confirmation:



Lead monoxide is easily reduced to the metal by heating with hydrogen, carbon monoxide, carbon, or potassium cyanide:

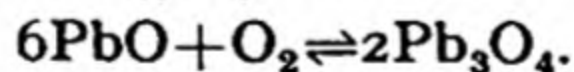


Lead hydroxide, $\text{Pb}(\text{OH})_2$, appears as a white gelatinous precipitate on addition of a caustic alkali to a solution of a lead salt:



Like the monoxide, it is amphoteric, yielding lead salts with acids and plumbites with alkalis.

Triplumbic tetroxide, red lead, or minium, Pb_3O_4 , is a red powder made by heating litharge in the air at about 400° . At a slightly higher temperature (about 470°) the reaction is reversed:

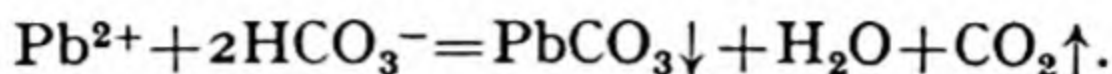


With dilute nitric acid at normal temperature, red lead yields lead nitrate (soluble) and lead dioxide, PbO_2 (insoluble). The ease with which this decomposition occurs might suggest that minium is a 'loose' compound or even a mixture of the monoxide and dioxide. X-ray examination of the three oxides PbO , Pb_3O_4 , and PbO_2 proves, however, that while the structure of minium contains

features similar to those of both monoxide and the dioxide, it must be regarded as a genuinely distinct compound.

Red lead is used as a pigment, and as an ingredient in the manufacture of 'crystal' glass (p. 411).

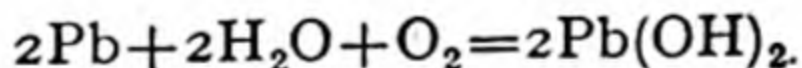
Lead carbonate, PbCO_3 , occurs naturally as *cerussite*. It can be obtained as a white precipitate by adding sodium bicarbonate solution to a cold solution of a lead salt:



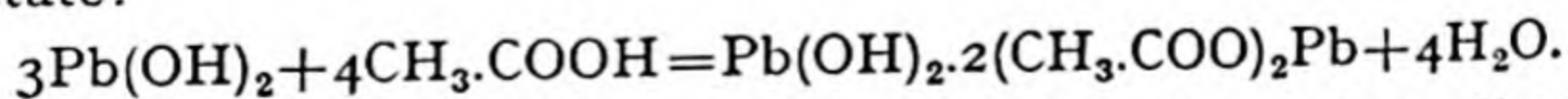
Sodium carbonate precipitates a basic lead carbonate, $\text{Pb}(\text{OH})_2 \cdot 2\text{PbCO}_3$, known as 'white lead.'

White lead is well known as the basis of lead paints, which are made by suspending it in linseed oil and turpentine, with the addition of suitable pigments if coloured paint is desired. It has good covering-power, especially when very finely divided, but it is poisonous, and slowly turns black in town air, since atmospheric hydrogen sulphide converts it into black lead sulphide, PbS . White lead is made in a variety of ways, e.g. electrolytically and by exposing sheets of lead to an atmosphere of carbon dioxide and acetic acid vapour at about 70° . The best-quality commercial white lead, in which the particles are extremely fine and which therefore has a very high covering-power, is made by the so-called Dutch process. In a brickwork 'stack' is placed a layer of horse dung or spent tannery bark. This ferments and keeps the stack warm, while carbon dioxide is formed as a product of the fermentation. On the fermenting layer are set a number of pots containing vinegar or dilute acetic acid, and perforated rolls of sheet lead are laid above them. Similar series of tannery bark, pots, and lead rolls are built upon the first series, until the stack is full.

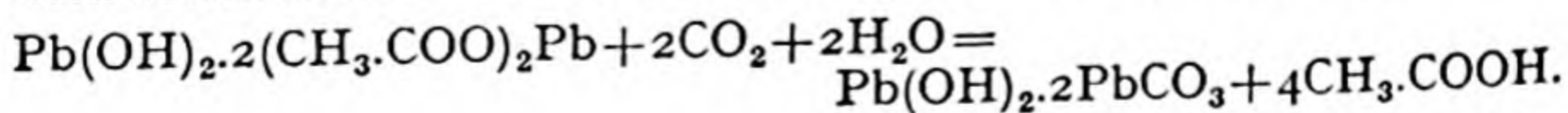
The reactions which result in the formation of white lead are not fully understood. It is likely that the lead is first converted into lead hydroxide:



and that this reacts with acetic acid vapour to form the basic acetate:



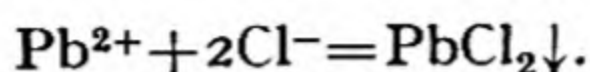
The basic acetate is then decomposed by the carbon dioxide, with formation of white lead and regeneration of acetic acid:



At the end of some three months, the stack is dismantled, and the white lead is removed, washed, and dried.

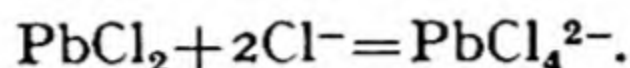
Lead chloride, PbCl_2 , is only slightly soluble in cold water and may

therefore be obtained by precipitation if the solutions are not too dilute:



The solubility increases with rise of temperature, but is appreciable even at room temperature.

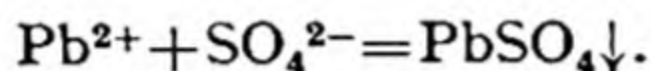
Lead chloride will also dissolve in concentrated hydrochloric acid, yielding the complex anion PbCl_4^{2-} :



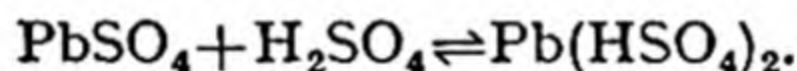
Lead bromide, PbBr_2 , is similar to the chloride.

Lead iodide, PbI_2 , is a yellow solid insoluble in cold water, but soluble in hot water to give a *colourless* solution, from which it crystallizes on cooling in beautifully lustrous golden spangles.

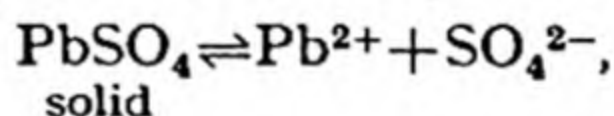
Lead sulphate, PbSO_4 , occurs native in Anglesey, whence its name *anglesite*. It is practically insoluble in water, and is prepared by precipitation:



Lead sulphate will dissolve in concentrated sulphuric acid, probably because the bisulphate is formed; on diluting the solution, the lead sulphate is precipitated:

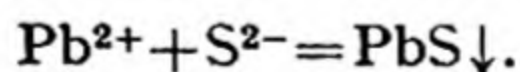


A property of lead sulphate used in qualitative analysis for the separation of the metal is its solubility in solutions of ammonium salts of certain organic acids, e.g. ammonium tartrate and acetate. This is explained by the fact that lead tartrate and acetate are only very slightly ionized, hence the equilibrium:

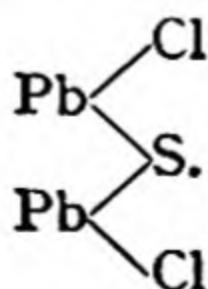


is disturbed by removal of Pb^{2+} ions, and more lead sulphate passes into solution.

Lead sulphide, PbS , occurs naturally as *galena*. It can be prepared synthetically, or by passing hydrogen sulphide into a solution of a lead salt:



In the last reaction, presence of excess of hydrochloric acid may cause the precipitation of the reddish-orange *sulphochloride*:



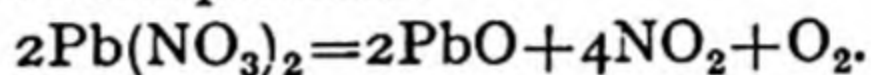
On dilution and further passage of hydrogen sulphide, however, this is converted into the black sulphide PbS.

Lead sulphide is insoluble in dilute hydrochloric acid, but dissolves in dilute nitric acid, forming lead nitrate; sulphur is deposited and nitric oxide is evolved:

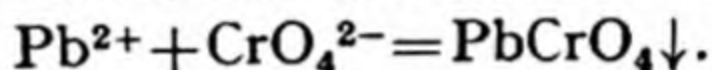


Lead sulphide is oxidized to white lead sulphate by hydrogen peroxide, a fact employed in restoring oil-paintings blackened by exposure to town air.

Lead nitrate, $\text{Pb}(\text{NO}_3)_2$, is an anhydrous colourless crystalline solid, prepared by the usual methods, and noteworthy as one of the comparatively few lead compounds readily soluble in water. On heating, it yields oxygen, nitrogen dioxide, and lead monoxide, with characteristic decrepitation:



Lead chromate, PbCrO_4 , is formed as a yellow precipitate by addition of potassium chromate solution to solution of a lead salt:



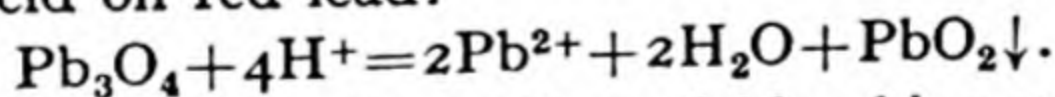
It is insoluble in acetic acid, but dissolves in solutions of caustic alkalis. Commercially it is used as a yellow pigment, *chrome yellow*.

Lead acetate, $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$, is prepared by dissolving lead monoxide in an excess of acetic acid, and concentrating the solution to the point of crystallization. Excess of lead monoxide gives *basic acetates*, solutions and ointments of which are used medicinally.

The normal acetate is popularly known as *sugar of lead*, on account of its sweet taste; it is, however, very poisonous.

COMPOUNDS OF LEAD: PLUMBIC COMPOUNDS

Lead dioxide, PbO_2 , is commonly prepared by the action of warm dilute nitric acid on red lead:



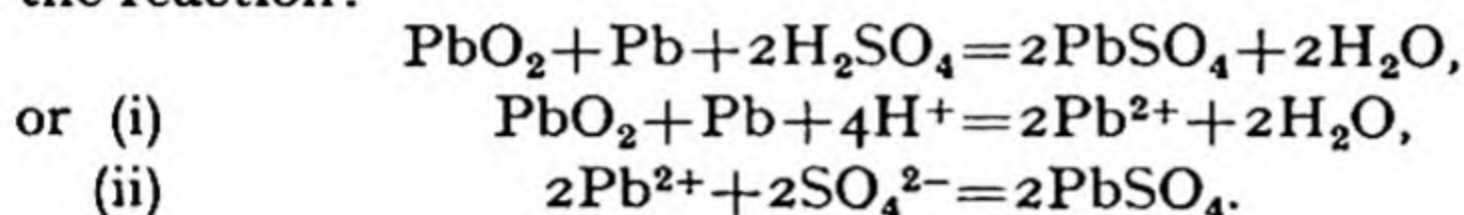
It may also be made by the action of bleaching-powder, sodium hypochlorite, or, better, hydrogen peroxide, upon a solution of litharge or lead hydroxide in aqueous alkali.

Lead dioxide is a brown powder — sometimes nearly black. When heated, it begins to decompose at about 300° , and is finally converted into litharge: $2\text{PbO}_2 = 2\text{PbO} + \text{O}_2 \uparrow$.

It is a very strong oxidizing agent. For example, it oxidizes hot concentrated hydrochloric acid to chlorine, phosphorus (explosively) to phosphoric oxide, sulphur dioxide to lead sulphate (with incandescence), and a manganous salt—in the presence of nitric acid—to permanganic acid.

Lead dioxide will dissolve not only in cold concentrated hydrochloric acid to form *chloroplumbic acid* (q.v.), but in concentrated (or fused) caustic alkali to form *metaplumbates*. These may be regarded as salts of *metaplumbic acid*, H_2PbO_3 , itself a hypothetical dehydration product of the hypothetical *orthoplumbic acid*, $\text{H}_2\text{Pb}(\text{OH})_6$. The metaplumbates are thermally more stable than lead dioxide.

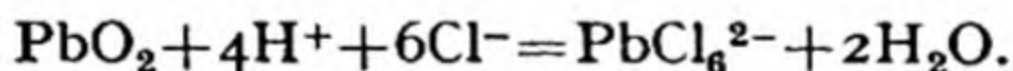
The *lead accumulator* consists of two lead plates or gratings immersed in 20 per cent aqueous sulphuric acid, the surface of one plate being covered with lead dioxide. The latter plate forms the positive pole of the cell, and when the two terminals are connected in a circuit a current flows, the necessary energy being provided by the reaction:



The plates thus become covered with lead sulphate, and sulphuric acid is removed from the solution, which becomes more dilute and of lower specific gravity.

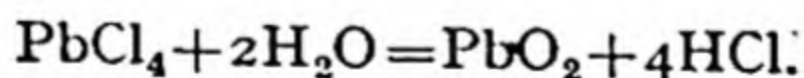
Recharge is effected by connecting the cell to a source of direct current, the current being made to flow in the opposite direction to that of the current given by the cell during use. The reverse changes then occur.

Plumbic chloride, lead tetrachloride, PbCl_4 , is prepared by dissolving lead dioxide in cold concentrated hydrochloric acid; the tetrachloride is thus formed in solution but combines with excess of hydrochloric acid to give a yellow substance, *chloroplumbic acid*, H_2PbCl_6 :



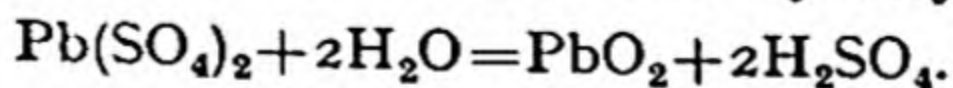
On addition of ammonium chloride, *ammonium chloroplumbate*, $(\text{NH}_4)_2\text{PbCl}_6$, separates as a yellow crystalline solid, and this, with cold concentrated sulphuric acid, yields plumbic chloride in the form of a yellow oily liquid (M.P. -15°).

Plumbic chloride is decomposed by water to form lead dioxide and hydrochloric acid:

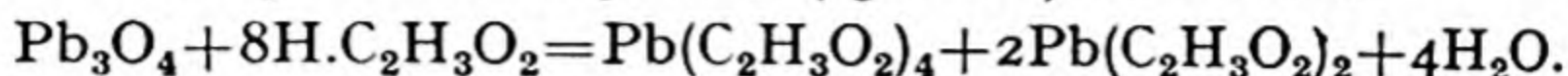


On heating it splits up into plumbous chloride and chlorine. It is a covalent substance (cf. SnCl_4 , SiCl_4).

Plumbic sulphate, $\text{Pb}(\text{SO}_4)_2$, is a yellowish-white crystalline solid obtained round the anode when cold 85 per cent sulphuric acid is electrolysed between lead electrodes. It is hydrolysed by water:

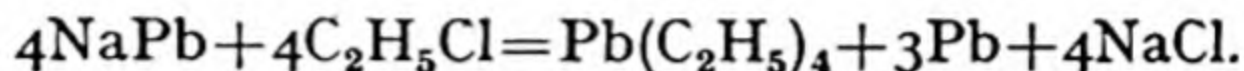


Lead tetra-acetate, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_4$. Red lead, but not lead dioxide, is dissolved by warm anhydrous ('glacial') acetic acid:



On cooling the solution only the tetra-acetate separates, as colourless crystals instantly decomposed by water to PbO_2 and acetic acid.

Lead tetra-ethyl, $\text{Pb}(\text{C}_2\text{H}_5)_4$, is a colourless, very poisonous liquid with a strong smell, made by treating sodium-lead alloy with ethyl chloride:



It is added to petrol ('ethyl' petrol) as an anti-knock. (Cf. p. 559).

Tests for Lead.

1. Charcoal block: grey metallic beads (Pb) which will mark paper.
2. Solutions of plumbous salts give with
 - (a) hydrochloric acid or a soluble chloride: white precipitate of lead chloride, PbCl_2 , soluble in hot water, insoluble in ammonia (which changes it to the basic chloride $\text{Pb}(\text{OH})_2.\text{PbCl}_2$);
 - (b) hydrogen sulphide: black precipitate of lead sulphide, PbS (q.v.);
 - (c) potassium chromate: yellow precipitate of lead chromate, insoluble in acetic acid;
 - (d) potassium iodide; yellow precipitate of lead iodide, soluble in boiling water;
 - (e) dilute sulphuric acid or a soluble sulphate: white precipitate of lead sulphate.

COMPARATIVE EXERCISES

1. Tabulate the principal points in which carbon and simple carbon compounds resemble silicon and simple silicon compounds.
2. Make a list of the properties in which the two elements and their compounds differ.
3. Revise Exercise 3 on p. 385.
4. Tabulate the principal points in which tin and tin compounds (a) resemble, and (b) differ from, lead and lead compounds.

CHAPTER XXVIII

GROUP V

NITROGEN, PHOSPHORUS, ARSENIC, ANTIMONY, BISMUTH

Nitrogen—Phosphorus $\left\{ \begin{array}{l} \text{Vanadium—Niobium—Tantalum} \\ \text{Arsenic—Antimony—Bismuth} \end{array} \right.$

The Nitrogen Family. The typical elements nitrogen and phosphorus are similar to the elements of Sub-group B, but show little resemblance to those of Sub-group A. Since all the elements in the series N—P—As—Sb—Bi are included in many Higher School syllabuses, the student is recommended to carry out the comparative exercises on p. 487 with even more than his usual care and diligence.

NITROGEN, N

Atomic number: 7. *Atomic weight:* 14.008. *Density (H=1):* 13.9.
Melting-point: -210° . *Boiling-point:* -195.8° .

History. Nitrogen was discovered in 1772 by D. RUTHERFORD, and independently—at about the same time—by PRIESTLEY and by SCHEELE. The name *nitrogen*, i.e. nitre-producer, was suggested by CHAPTAL.

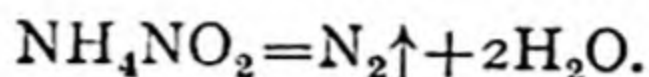
Occurrence. Elementary nitrogen occurs in the air, of which it forms about 78 per cent by volume. The principal deposit of a nitrogen compound is found in Chile, where large quantities of Chile saltpetre—crude *sodium nitrate*, NaNO_3 , p. 297—are mined every year. Nitrates and other nitrogenous substances are present in all fertile soil, and in the sea, while protoplasm contains nitrogen as one of its essential constituents.

Industrial Preparation. Nitrogen is obtained industrially by the fractional distillation of liquid air, a process described on p. 488. It is also obtained from producer-gas (p. 396) by mixing the latter with steam and passing the mixture through a heated catalyst (cf. p. 431). The resulting gases—nitrogen, hydrogen, and carbon dioxide—are freed from carbon dioxide by agitation with water under pressure, and the nitrogen-hydrogen mixture is then usually enriched with sufficient additional hydrogen to render it suitable for the HABER synthesis of ammonia (p. 431).

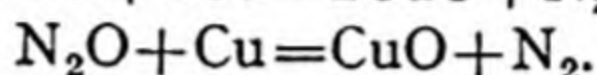
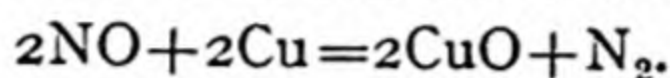
Laboratory Preparation. Nitrogen contaminated with the inert gases can be prepared from the atmosphere by passing a current of

air through caustic soda solution, to remove carbon dioxide, and then over heated copper, to remove oxygen.

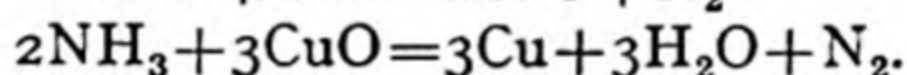
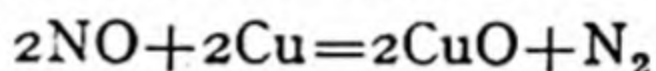
A more convenient method of preparing nitrogen is to heat a solution of ammonium nitrite (for which a mixture of sodium nitrite and ammonium chloride is usually substituted, since ammonium nitrite is unstable):



The gas so prepared is liable to contain ammonia and oxides of nitrogen as impurities. A purer specimen can be obtained by heating copper in pure nitric or nitrous oxide:

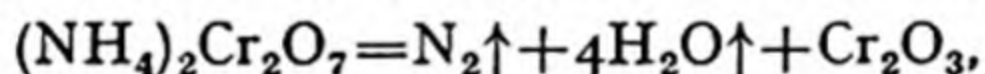


A very convenient method of continuous production is to form a mixture of nitric oxide and ammonia by passing the former gas through concentrated aqueous ammonia, and then to pass the mixture over heated copper, which, owing to the reducing action of the ammonia, remains unoxidized:

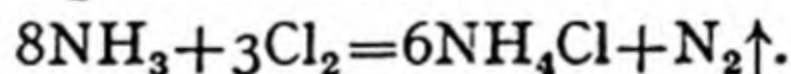


The net action is, therefore, the oxidation of ammonia by nitric oxide, with copper as catalyst. Excess of ammonia is easily removed by passing the treated gas through acid.

Nitrogen is liberated when ammonium dichromate is heated:



and when chlorine is passed into *excess* of ammonia solution:



Excess of chlorine must be avoided, since the dangerously explosive *nitrogen trichloride*, NCl_3 , may be formed (p. 456).

Properties. Nitrogen is a colourless, tasteless, and odourless gas, non-poisonous but unable to support respiration. It melts at -210° , boils at -195.8° , and is somewhat less dense than air. It is slightly soluble in water, 1 c.c. of which dissolves 0.024 c.c. of the gas at 0° .

Under the usual conditions of the laboratory, nitrogen is chemically unreactive; at high temperatures and pressures, however, it will combine directly with oxygen, to form oxides, and with hydrogen, to form ammonia (p. 429). Certain elements form *nitrides* if heated in nitrogen; they include calcium, strontium, barium, magnesium, manganese, and boron.

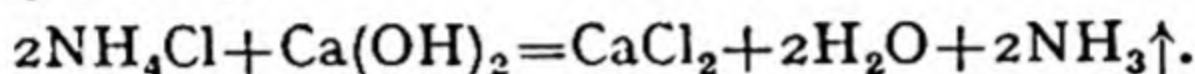
Active nitrogen, prepared by passing a silent electric discharge through gaseous nitrogen containing traces of oxygen, and at low pressure, shows a yellow luminescence and is chemically active. The nature of active nitrogen has not yet been elucidated.

HYDRIDES OF NITROGEN

Nitrogen forms two basic hydrides, viz. *ammonia*, NH_3 , and *hydrazine*, NH_2NH_2 ; and one acidic hydride, viz. *hydrazoic acid*, HN_3 . Since hydrazoic acid forms salts with both ammonia and hydrazine, the additional hydrides NH_3HN_3 , *ammonium azide*, and $\text{N}_2\text{H}_4\text{HN}_3$, *hydrazine azide*, may be included.

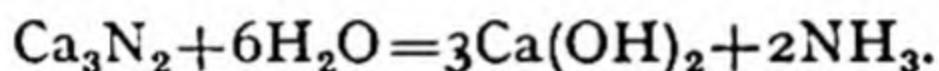
Ammonia, NH_3 , is among the most vital of all substances, whether in peace or in war, since it is a source of both fertilizers and explosives. It is manufactured on such an enormous scale that occasion seldom arises to prepare it in the laboratory; but it can, if necessary, be obtained in the following ways, among others:

(i) By heating an ammonium salt with an alkali, e.g. slaked lime or sodium hydroxide:

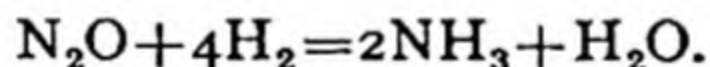


The gas is dried with quicklime and collected over mercury, or by passing it upwards into an inverted gas-jar, since it is less dense than air.

(ii) By the action of water on calcium nitride or magnesium nitride:



(iii) By the reduction of oxides of nitrogen with hydrogen in the presence of a heated catalyst, e.g. reduced nickel, platinum black, palladium black:

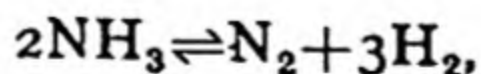


Industrially ammonia is formed as an impure aqueous solution ('gas-liquor') in the manufacture of coal-gas (p. 392). The solution is heated with slaked lime to drive off the ammonia, which is collected in dilute sulphuric acid as *ammonium sulphate*, $(\text{NH}_4)_2\text{SO}_4$. This was formerly the chief source of ammonia and ammonium salts, but is now of only minor importance. In modern practice, ammonia is manufactured synthetically.

SYNTHESIS OF AMMONIA

[N.B.—The conversion of gaseous nitrogen into nitrogenous compounds is called 'fixation of nitrogen.']

General. It was observed by REGNAULT in 1840 that when hydrogen and nitrogen are sparked together small quantities of ammonia are formed, while in 1865 DEVILLE showed that the decomposition of ammonia by sparks is never quite complete. Hence the reaction:



is a reversible one. The equilibrium mixture obtained under

ordinary conditions of sparking contains 2–3 per cent of ammonia and 97–98 per cent of uncombined hydrogen and nitrogen. If the ammonia is removed as soon as it is formed, e.g. by conducting the experiment over concentrated sulphuric acid, prolonged sparking will cause the complete combination of a mixture of 1 volume of nitrogen and 3 volumes of hydrogen.

It will be observed from the above equation that, in the formation of ammonia from hydrogen and nitrogen, a contraction in volume occurs; hence by the principle of LE CHATELIER (p. 130) *increase of pressure will increase* the proportion of ammonia in the equilibrium mixture. On the other hand, since ammonia is an exothermic compound (at least up to temperatures of 1,000°) with a heat of formation of about –11 kcal., *rise in temperature will lower* the proportion of ammonia in the equilibrium mixtures. The following table shows the percentage of ammonia at equilibrium under various conditions of temperature and pressure:

Temp. ° C.	Pressure in Atmospheres					
	1	10	100	300	600	1,000
250		28.3	67.2	81.4	90.7	96.2
300		14.7	52.0	71.0	84.2	92.6
400		3.85	25.1	47.0	65.2	79.8
450		2.1	16.4	35.8	53.7	69.7
500		1.2	10.6	26.4	42.2	57.5
600		0.5	4.5	13.8	23.1	31.4
700	0.02	0.23	2.2	7.3	12.6	12.9
1000	0.005					

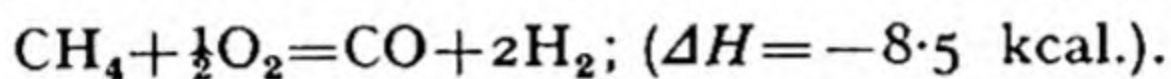
The value of the equilibrium constant, K , at any particular temperature, may be calculated from the equation:

$$K = \frac{[\text{NH}_3]^2}{[\text{H}_2]^3[\text{N}_2]}$$

The temperatures at which the yield of ammonia is commercially profitable are so low that the time taken to reach equilibrium is very great; hence attempts were early made to effect the combination more speedily by means of catalysts. In 1881 TELLIER proposed to use spongy iron for the purpose, while in 1895 HLAVATI patented the use of a mixture of titanium and platinum. It was not until 1913, however, that the problem was solved on the industrial scale, thanks to the labours of F. HABER and the technical resources of the wealthy German chemical firm, the Badische Anilin- und Soda-fabrik.

The Haber Process. After about 1920 the large-scale synthesis of ammonia from its elements was adopted as the principal means of nitrogen 'fixation' by nearly all industrial countries. Apart from

variations in the sources of hydrogen the Haber process, with only minor differences in technique, has come to be very widely if not universally employed. The pressure of operation varies only between 200 and 350 atmospheres and the temperature from 350° to 500° ; the catalyst is essentially finely divided iron reduced from oxide *in situ* by hydrogen in the reaction gas mixture. In countries with a large petroleum industry, such as the U.S.A., abundant hydrogen is obtained from (a) refinery gas, and (b) natural gas. Refinery gas, collected during the chemical treatment of petroleum, may contain as much as 70 volume per cent of hydrogen, which is purified from the liquefiable admixtures by refrigeration. Natural gas, which is mainly methane, is submitted to partial combustion, in which carbon is oxidized first and hydrogen freed:



In 1957 in the U.S.A. 72 per cent of the hydrogen used in ammonia synthesis was produced from natural gas in this way. A similar process is increasingly applied to fuel oils, which contain a complex mixture of hydrocarbons.

Synopsis of the Haber Process as worked in the United Kingdom.

(1) Hydrogen and nitrogen (with carbon monoxide and dioxide) produced as semi-water-gas from steam, coke, and air. As explained on p. 396, the water-gas reaction is endothermic, and the necessary temperature in the coke bed is maintained by alternating steam with air 'blows.' During the early part of the latter the gas is mainly carbon dioxide and nitrogen and is blown to waste. As the temperature of the coke rises to a maximum in the later part of the 'blow' carbon monoxide largely replaces dioxide and the gas mixture is collected and added to the steam blow gas in such proportion that after the Bosch reaction in stage (3) the required 3 : 1 ratio of hydrogen to nitrogen is attained. The average final composition of the semi-water-gas is:

H_2	N_2	CO	CO_2	H_2S	
39	21	32	7	0.2	(by volume).

(2) Sulphur removed by iron oxide (as in gas-works practice, q.v.).

(3) Bosch reaction to increase the proportion of hydrogen at the expense of carbon monoxide (p. 275). At this stage the gas composition is approximately:

H_2	N_2	CO_2	CO	
51	17	26.5	4.5	(by volume).

(4) Compression to 50 atmospheres pressure.

(5) Carbon dioxide removed by water scrubbing in counter-current operation.

(6) Compression to 250 atmospheres pressure.

(7) Carbon monoxide removed by 'copper liquor' containing the diammino-cuprous cation:



carbon monoxide recovered by heating the spent liquor is passed back to the Bosch operation (3).

(8) Synthesis of ammonia in converter with catalyst.

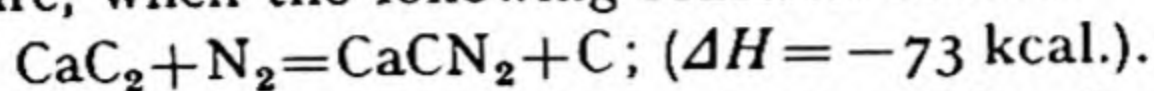
(9) Ammonia removed from the circulating gas mixture by cooling and condensation, and stored as liquid ammonia (B.P. -33°).

The Iron Catalyst. A paste consisting of magnetic iron oxide, Fe_3O_4 , with a small amount of alumina, and moistened with potash liquor, is dried and then heated to fusion at a high temperature. The cooled solid is broken up and sieved into uniform pea-sized pellets, which occupy most of the internal capacity of the converters, each of which is charged with about 100 cubic feet, or 7 tons, of the pellets.

For industrial purposes the *endurance* of a catalyst is as important as its activity. It was found that iron reduced from its pure oxides had a high initial activity, but this was very short-lived. It is the role of the admixed alumina to prolong the activity, which in the synthesis operated in the U.K. is maintained for at least a year. In the fusion of the catalyst mixture ferrous 'aluminate,' FeAl_2O_4 , is formed and this compound is isomorphous with magnetic oxide Fe_3O_4 (compare $\text{Fe}^{\text{II}}(\text{Fe}^{\text{III}})_2\text{O}_4$ with $\text{Fe}^{\text{II}}(\text{Al}^{\text{III}})_2\text{O}_4$), so that the final mixture contains Fe_3O_4 with a small amount of aluminate uniformly distributed in solid solution. After reduction each iron particle is isolated from others surrounding it by a film of the irreducible alumina, and the cause of the loss of activity, that is the spontaneous and progressive sintering of the finely divided iron into coarser particles of greatly reduced surface, is removed.

The Converter. The 25-feet-high cylindrical pressure vessels of tungsten steel (p. 615) have an outside diameter of about 5 feet, and walls 6–7 inches thick: each vessel weighs about 100 tons. The central space is filled with the bed of catalyst pellets, the temperature of which is registered by means of a thermocouple reaching within it. The catalyst is surrounded by coiled heat interchange piping built into the inner surface of the converter, through which the entering gas mixture passes. The very important control of the temperature within the catalyst bed is effected by means of this heat interchange system. The exit gas at about 200° and 200 atmospheres pressure and containing 10–20 per cent of ammonia is cooled to ordinary temperature by external water cooling, when most of the ammonia liquefies and is run off into store. The remaining gas with about 5 per cent of residual ammonia is re-cycled by mixing with new gas entering the converter.

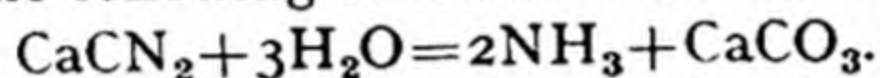
The Cyanamide Process. An entirely different method of synthesizing ammonia was worked out during the years 1895-1901 by FRANK and CARO. Finely ground calcium carbide, CaC_2 , with a trace of calcium fluoride as catalyst, is heated in pure nitrogen under slight pressure, when the following reaction occurs:



The change is strongly exothermic, and when it has been started by means of a carbon rod heated electrically it proceeds spontaneously, the temperature of the oven remaining at about $1,000^\circ$. A single oven may hold as much as a ton of the carbide, and the time taken for the conversion is one to two days.

The product, known as 'cyanamide,' or 'nitrolim,' is a greyish-black mass consisting of a mixture of *calcium cyanamide*, CaCN_2 , and graphite. It is finely ground and treated with a spray of water to remove small quantities of unchanged carbide always present in it, after which it is used directly as a fertilizer or as a source of ammonia.

For the second purpose, it is heated with 3 per cent sodium hydroxide solution in strong iron vessels ('autoclaves') until the temperature rises well above 100° and the pressure reaches 3 or 4 atmospheres. The following reaction then takes place:

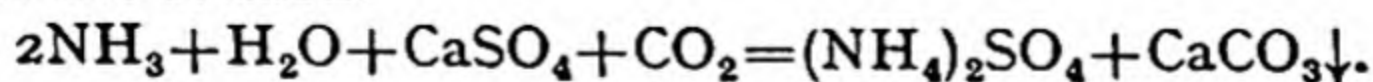


The reaction is exothermic, and this, together with the formation of ammonia, causes the pressure to rise rapidly; ammonia and steam are therefore blown off from the autoclaves at intervals.

Calcium cyanamide, although an ionic compound, $\text{Ca}^{2+}(\bar{\text{N}}=\text{C}=\bar{\text{N}})^{2-}$, is a derivative of *cyanamide*, NH_2CN , which may itself be regarded as the amide of *cyanic acid*, HO.CN . Other derivatives, e.g. *sodium cyanamide*, Na_2CN_2 , and the yellow *silver cyanamide*, Ag_2CN_2 , are known. The use of calcium cyanamide as a fertilizer depends upon the fact that the moisture in the soil converts it successively into urea, $\text{CO}(\text{NH}_2)_2$, and ammonium carbonate, both of which can be assimilated by plants:

- (i) $\text{CaCN}_2 + 3\text{H}_2\text{O} = \text{Ca}(\text{OH})_2 + \text{CO}(\text{NH}_2)_2$.
- (ii) $\text{CO}(\text{NH}_2)_2 + 2\text{H}_2\text{O} = (\text{NH}_4)_2\text{CO}_3$.

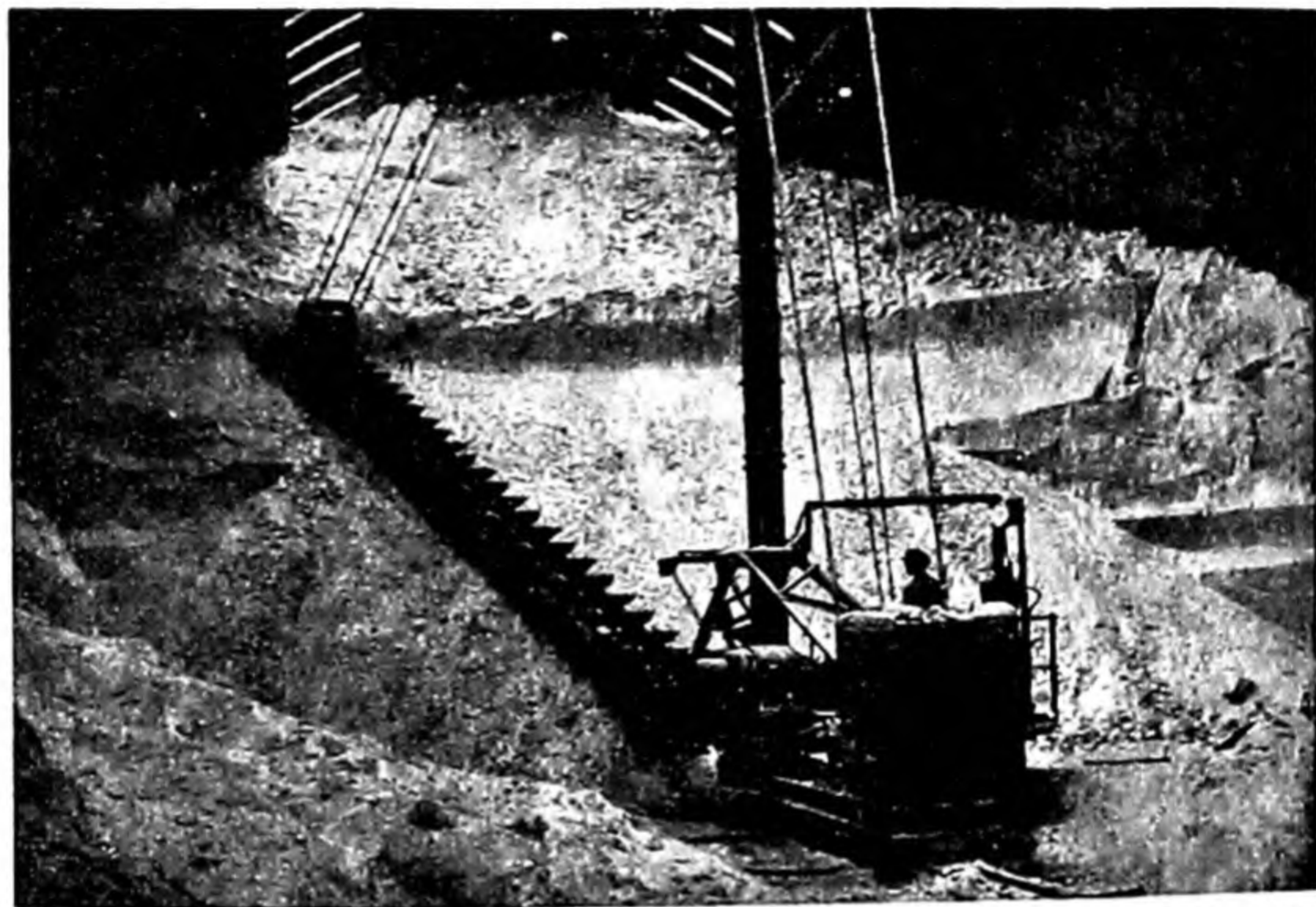
Manufacture of Ammonium Sulphate. Finely powdered calcium sulphate, CaSO_4 , is stirred up in ammonia solution, and carbon dioxide is then blown in, when ammonium sulphate and calcium carbonate are formed:



The precipitate of calcium carbonate is removed and the solution of ammonium sulphate ('sulphate of ammonia') is evaporated. The

calcium carbonate always retains a little ammonium sulphate, and is therefore especially suitable for agricultural purposes; it is sold as a fertilizer under the name of 'agricultural chalk.'

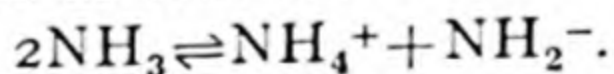
Properties of Ammonia. Ammonia is a colourless gas with a pungent and suffocating smell. It is only about half as dense as air. Since it has a high critical temperature (132.4°), it can be condensed to a liquid at ordinary temperatures by the application of



Imperial Chemical Industries Ltd.

FIG. 80. AMMONIUM SULPHATE READY FOR PACKING

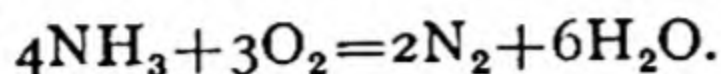
increased pressure; the liquid boils at -33.5° , freezes at -78° , and is a good ionizing solvent, i.e. many electrolytes dissolve in it to give solutions which contain ions and are therefore conductors. It is itself slightly ionized as follows:



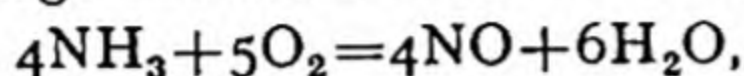
Liquid ammonia is used as a conveniently transportable form of hydrogen, since it can easily be 'cracked' into its constituent elements and the cost of carrying hydrogen as liquid ammonia is much less than the cost of carrying the gas in steel cylinders.

Ammonia is extremely soluble in water, 1 c.c. of which dissolves some 1,300 c.c. of the gas at 0° . Saturated ammonia solution at 15° contains about 36 per cent NH_3 ; '8-80 ammonia,' i.e. a solution of specific gravity 0.880, contains 35 per cent NH_3 , and is thus approximately 20-N. Ammonia will also dissolve in many organic solvents, e.g. alcohol.

Ammonia readily burns in oxygen, and in air if previously heated; the flame is of a peculiar yellowish-brown colour and resembles that of burning methylamine. The main products of combustion are nitrogen and water:



In the presence of a heated catalyst, e.g. platinum, ammonia and air (or oxygen) undergo the exothermic reaction:



sufficient heat being evolved to maintain the platinum at a red heat. This reaction is used in the manufacture of nitric acid (p. 447).

Except in the complete absence of moisture, ammonia will combine directly with acids to form *ammonium salts*, e.g. NH_4Cl . Most of these dissociate on heating, but some decompose in other ways.

Towards oxidizing agents, ammonia is fairly stable, but it will reduce many metallic oxides to metal on heating.

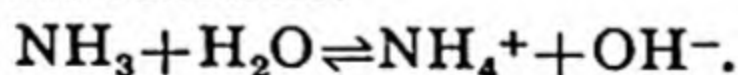
Sodamide, NaNH_2 , and *potassamide*, KNH_2 , are obtained as white solids when the metals are heated in gaseous ammonia. Sodamide is a useful reagent, and is of importance in the manufacture of explosives.

The *composition of ammonia* may be established as follows. If 2 volumes of ammonia are sparked until no further increase in volume occurs, it is found that 4 volumes of a mixture of nitrogen and hydrogen are formed. On adding excess of oxygen and exploding, a diminution in volume occurs of which two-thirds represents the volume of hydrogen in the nitrogen-hydrogen mixture. The volume of hydrogen thus determined proves to be three-quarters of the total volume of mixed nitrogen and hydrogen. Hence:

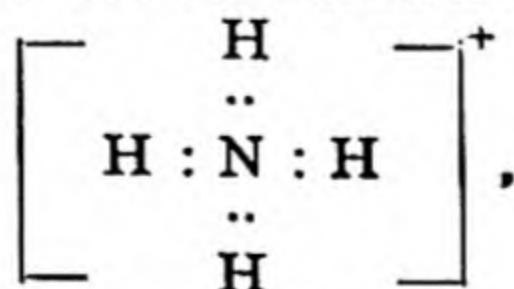
2 vols. ammonia give 1 vol. nitrogen + 3 vols. hydrogen,

\therefore by AVOGADRO'S principle, 1 molecule of ammonia consists of half a molecule of nitrogen and $1\frac{1}{2}$ molecules of hydrogen, and its formula is thus NH_3 .

Ammonia as a Base: Ammonium Salts. A solution of ammonia in water behaves as a weak electrolyte, and is alkaline to litmus, owing to the reversible reaction:



The electronic structure of the ammonium ion

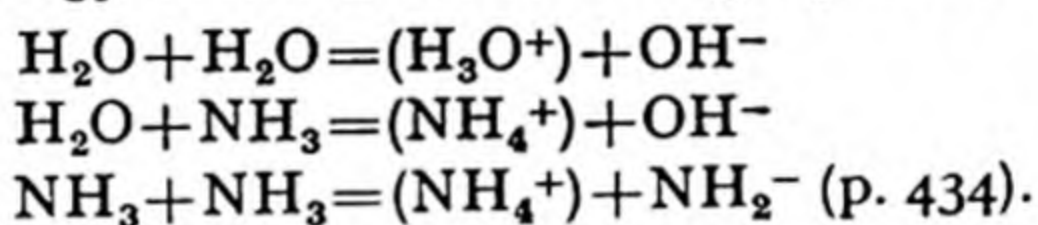


shows that all the eight contained electrons are fully occupied in bonding.

Moreover nitrogen, having in its valency zone only four orbitals ($2s, 2p_3$), cannot accommodate in that zone more than four electron pairs. Hence normal *covalent* compounds of the type NH_4X cannot exist. In particular, the so-called 'ammonium hydroxide' cannot be a covalent compound of normal type. It is, however, possible that hydroxyl ion could be loosely attached to ammonium ion by means of the so-called 'hydrogen bond.' Since the only electrons associated with hydrogen in ammonia are also shared by nitrogen, the proton is very 'exposed' and by *electrostatic attraction* can bind hydroxyl ion (see p. 118). In pure aqueous ammonia, only the concentrations $[\text{NH}_3]$, $[\text{NH}_4^+]$, and $[\text{OH}^-]$ (the latter being equal) can be determined: the *basic constant* is expressed as

$$\frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = K_b.$$

Logically, K_b should not be termed a 'dissociation' constant (p. 219). The analogy between the following equations is noteworthy:



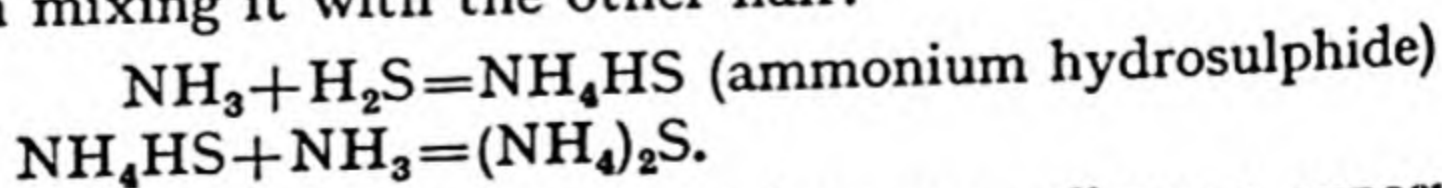
Ammonia solution neutralizes acids, forming the corresponding ammonium salts, and precipitates the hydroxides of many metals from solutions of the metallic salts. Its use in analysis is discussed on p. 228. On boiling, it loses all its ammonia, no constant-boiling mixture being formed (contrast hydrogen chloride, p. 549).

For 'ammonium'-amalgam, see p. 364.

Ammonium chloride, or 'sal ammoniac,' NH_4Cl , is a colourless crystalline solid which sublimes on heating. The vapour is dissociated. Sal ammoniac is the electrolyte in LECLANCHÉ cells of both wet and dry types.

Ammonium sulphate, 'sulphate of ammonia,' $(\text{NH}_4)_2\text{SO}_4$, obtained as described on p. 433, is an important fertilizer. On careful heating, it loses ammonia and is converted into the bisulphate, $(\text{NH}_4)\text{HSO}_4$, which is itself dissociated into ammonia and sulphuric acid at higher temperatures.

Ammonium sulphide, $(\text{NH}_4)_2\text{S}$, is obtained in solution by saturating half a given volume of ammonia solution with hydrogen sulphide and then mixing it with the other half:



The solution is colourless, but soon becomes yellow on exposure to air, since sulphur is liberated by oxidation and dissolves in the unchanged sulphide to form yellow *ammonium polysulphides*, e.g.

$(\text{NH}_4)_2\text{S}_5$. Solutions of these compounds are used in qualitative analysis.

Ammonium carbonate. The white substance contained in the laboratory reagent-bottles bearing this name is largely a mixture of ammonium bicarbonate, NH_4HCO_3 , with *ammonium carbamate*, $\text{NH}_2\text{COONH}_4$; it contains little of the normal carbonate, $(\text{NH}_4)_2\text{CO}_3$. The commercial method of preparation is to sublime it from a mixture of calcium carbonate and ammonium sulphate.

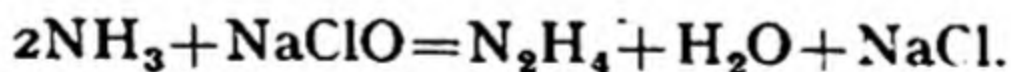
Ammonium nitrate, NH_4NO_3 , is important as an ingredient of many explosives (e.g. amatol—a mixture of NH_4NO_3 and T.N.T.), as a fertilizer, and as a source of nitrous oxide (p. 439), which it yields on heating.

Ammonium perchlorate, NH_4ClO_4 , is also used in the explosives industry. It shares with the nitrate the advantage of leaving no solid residue after explosion.

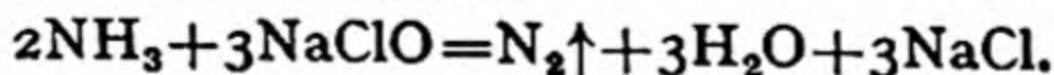
Tests for Ammonia and Ammonium Salts.

1. The smell of ammonia is almost unmistakable, though it closely resembles that of the lower aliphatic amines. Ammonium salts yield ammonia on heating with alkali.
2. NESSLER'S solution (p. 368) gives a yellow coloration or orange-brown precipitate with ammonia or an alkaline solution of an ammonium salt.
3. Ammonia with copper sulphate solution yields a pale blue precipitate of copper hydroxide, which dissolves in excess of ammonia solution to give a deep blue liquid (p. 319).

Hydrazine, N_2H_4 or $\text{H}_2\text{N.NH}_2$, is obtained by oxidizing an aqueous solution of ammonia, containing a little gelatine, with sodium hypochlorite (see also p. 456). The resulting liquid is concentrated by evaporation, cooled and acidified with sulphuric acid, when colourless crystals of *hydrazine sulphate*, $\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4$, are deposited:



The effect of the gelatine is to de-activate traces of metallic impurities, particularly copper and ferric compounds, which catalyse the alternative reaction:

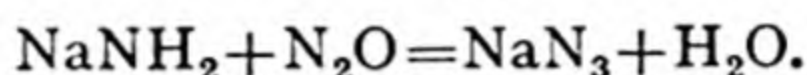


Hydrazine is a di-acid base. It can be liberated from its salts by distilling them with caustic soda solution under reduced pressure; the distillate is a colourless liquid (B.P. 119°) with an ammoniacal smell and is the stable *hydrate*, $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$. Anhydrous hydrazine is readily obtained (as a colourless liquid, B.P. 113.5°) by mixing

its sulphate with liquid ammonia, allowing the excess of ammonia to boil off, and then decanting from the solid ammonium sulphate.

Hydrazine attacks rubber, cork, and glass, and takes fire spontaneously in oxygen. It is a powerful reducing agent. Its derivatives, *phenylhydrazine*, $C_6H_5.NH.NH_2$, and *para-nitro-phenylhydrazine*, $C_6H_4(NO_2).NH.NH_2$, are used in organic chemistry in the investigation of substances containing the carbonyl group, $>CO$.

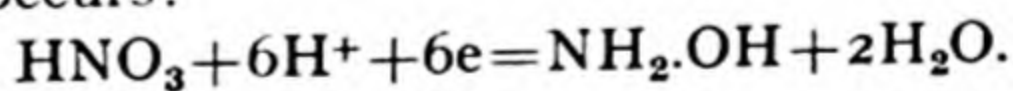
Hydrazoic acid, HN_3 , is made by distilling its sodium salt, NaN_3 , with dilute sulphuric acid. Sodium azide is prepared by heating sodamide (p. 287) in dry nitrous oxide at 190° :



Hydrazoic acid is a colourless liquid with an unpleasant smell. It boils at 37° and may explode if heated to a higher temperature. It is very poisonous. Of its salts the *azides*, lead azide, $Pb(N_3)_2$, has some importance as a detonator.

A constitution $H.N \begin{array}{c} \diagup N \\ || \\ \diagdown N \end{array}$ was formerly ascribed to hydrazoic acid, but X-ray examination of azides proved that in the azide ion N_3^- the centres of the three atoms lie in a straight line, i.e. in a *linear* structure, with formula $\bar{N}=\overset{+}{N}=\bar{N}$, which is isoelectronic with the cyanamide ion (p. 433).

Hydroxylamine, $NH_2.OH$, can be prepared by various chemical methods, e.g. by reducing nitric acid or nitric oxide with tin and hydrochloric acid. It is, however, usually obtained electrolytically. Fairly concentrated (1 : 1) sulphuric acid is electrolysed between a platinum anode and a lead cathode separated by a porous diaphragm (e.g. a porous pot). Dilute nitric acid or a dilute solution of a nitrate is introduced into the cathode chamber, and the following reaction occurs:



Hydroxylamine is a colourless crystalline solid, which on heating melts at 33° (unless, as very often happens, it explodes first). It is a basic substance and is generally employed in the form of its salts, e.g. *hydroxylamine hydrochloride*, $NH_2.OH.HCl$, which are much more stable. An aqueous solution of the free base is easily prepared by dissolving one of the salts in water and adding caustic soda.

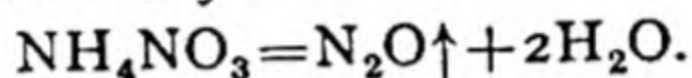
Both hydroxylamine and its salts are powerful reducing agents. In organic chemistry, hydroxylamine is employed to form the *oximes* of aldehydes and ketones.

OXIDES OF NITROGEN

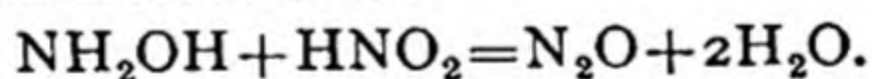
Nitrogen forms five oxides, which, with the oxyacids corresponding to them in formula, though not necessarily in structure, are shown below:

<i>Oxide</i>	<i>Acid</i>
Nitrous oxide, N_2O	Hyponitrous acid, $H_2N_2O_2$
Nitric oxide, NO	
Nitrous anhydride, N_2O_3	Nitrous acid, HNO_2
Nitrogen dioxide, NO_2	{ Nitrous acid, HNO_2 Nitric acid, HNO_3
Nitrogen pentoxide, N_2O_5	Nitric acid, HNO_3

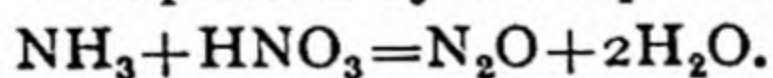
Nitrous oxide, N_2O . Nitrous oxide was discovered in 1772 by PRIESTLEY. In 1793 DEIMAN showed that it could be prepared by heating ammonium nitrate, and this is the method generally employed at the present day:



The ammonium nitrate should be free from ammonium chloride, and the heating should not be too vigorous or too prolonged, or explosions may occur. The gas is collected over brine or hot water since it is soluble in cold water. If required pure, it may be passed through an aqueous solution of ferrous sulphate, which removes the traces of nitric oxide (p. 441) invariably present, and then through concentrated sulphuric acid to remove water-vapour; the pure dry gas is collected over mercury. In the laboratory the most convenient method of preparation uses the reaction between hydroxylamine and nitrous acid:

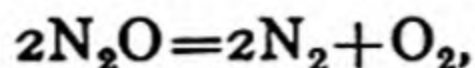


A concentrated solution of sodium nitrite is dropped slowly into a cold solution of hydroxylamine hydrochloride, when nitrous oxide is immediately released in a brisk effervescence. It is interesting to compare this method with the older one employing ammonium nitrate, which may be expressed by the equation

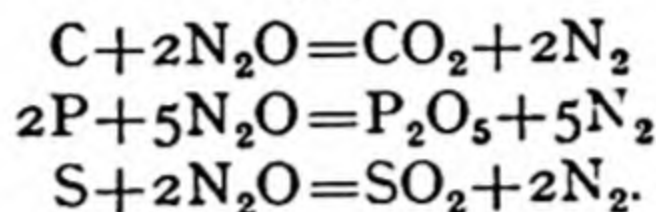


Properties. Nitrous oxide is a colourless gas with a sweetish taste and smell. These it imparts to cold water, in which it is fairly soluble, water dissolving about two-thirds of its own volume of nitrous oxide at 20° . It is easily liquefied, the liquid freezing at -91° and boiling at -89° . It is an endothermic substance, its heat of formation being 19.65 kcal. At a red heat, c. 700° , it is

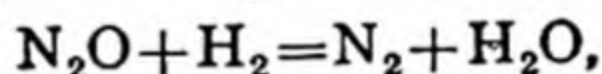
decomposed into its elements, and since the resulting mixture of gases contains one-third of its volume of oxygen:



nitrous oxide vigorously supports the combustion of any burning substance hot enough to decompose it. The combustion is assisted by the heat given out during the decomposition, viz. 19.65 kcal. per gram-molecule. Feebly burning substances may be extinguished in it, but it will relight a small bundle of glowing splints (the test usually fails with a single splint). In general the gas supports combustion nearly as well as oxygen:

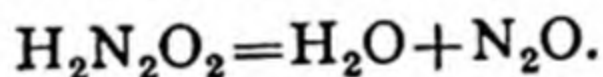


Within certain limits of proportion by volume, a mixture of hydrogen and nitrous oxide explodes if ignited:



but hydrogen will burn quietly in an atmosphere of nitrous oxide and the flame is luminous enough to read by.

From its formula, nitrous oxide might be regarded as the anhydride of hyponitrous acid, $\text{H}_2\text{N}_2\text{O}_2$. Its solution in water, however, is not acid, and in all respects it behaves as a neutral oxide. On the other hand, nitrous oxide can be obtained by the dehydration of hyponitrous acid with concentrated sulphuric acid:



Distinction from Oxygen. The fact that both gases relight glowing splints may occasionally cause oxygen to be confused with nitrous oxide, though the dissimilarity between them is so great that a list of distinguishing tests is almost superfluous:

- (a) Nitrous oxide has a taste and smell; oxygen has neither.
- (b) Nitrous oxide is soluble in cold water.
- (c) Nitrous oxide will not form nitrogen dioxide when brought into contact with nitric oxide; oxygen will.
- (d) The density of nitrous oxide is 22; that of oxygen is 16.
- (e) Nitrous oxide has a peculiar physiological action, considered in the next paragraph.

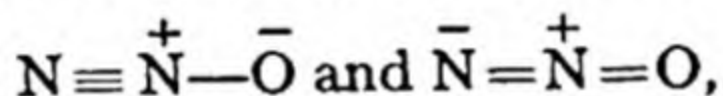
Physiological Action of Nitrous Oxide. When inhaled, nitrous oxide first produces a feeling of exhilaration and excitement, and occasionally gives rise to uncontrollable laughter; hence its popular name of 'laughing gas.' Further inhalation causes hallucinations, often of a very pleasurable nature, so that the French call it *gaz du*

paradis; but the hallucinations quickly give place to anaesthesia and the *gaz du paradis* is now serving as *gaz de l'enfer*, or 'dentist's gas.' If the administration is continued too long, the anaesthesia ends in death; but among general anaesthetics nitrous oxide is considered to be one of the safest.

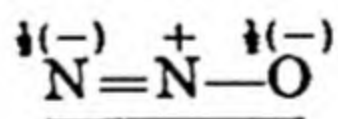
Though it can be breathed without discomfort, nitrous oxide will not support life, therefore when it is used for anaesthetic purposes oxygen is mixed with it. SIR HUMPHRY DAVY inhaled 15 quarts of the pure gas and danced about the laboratory as a madman.

Constitution. On continued sparking, 1 volume of nitrous oxide yields $1\frac{1}{2}$ volumes of mixed oxygen and nitrogen, and by the addition of alkaline pyrogallol to the mixture the volume of oxygen can be found by observing the diminution that occurs; it proves to be half a volume.

Formerly the cyclic formula $\begin{array}{c} \text{N} = \text{N} \\ \diagdown \quad \diagup \\ \text{O} \end{array}$ was accepted, but modern methods of discovering the shapes of molecules have proved that the centres of the three atoms lie in one straight line, in the order NNO. If all bonding electrons were assumed to be localized between two atoms *two* electronic formulae could be written:

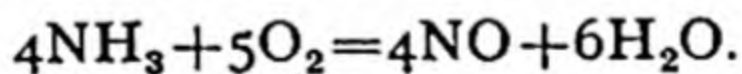


which condense to one if one pair of bonding electrons is 'delocalized' over the whole molecule:

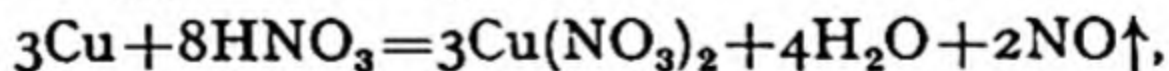


(cf. p. 120).

Nitric oxide, NO. Nitric oxide is prepared industrially by the catalytic oxidation of ammonia (cf. p. 447):



In the laboratory it is prepared by the action upon copper of cold concentrated nitric acid diluted with its own volume of water. The reaction is approximately:

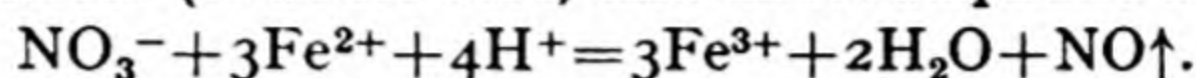


but side-reactions invariably occur, resulting in the formation of nitrogen, nitrous oxide, and nitrogen dioxide. The nitric oxide is purified by passing the mixture of gases into a solution of ferrous sulphate, with which it forms a dark brown compound, $\text{FeSO}_4 \cdot \text{NO}$. On boiling the solution, this substance decomposes and pure nitric oxide comes off. It may be collected over water, or, if required dry,

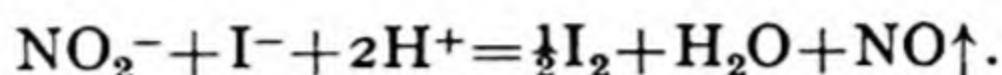
over mercury after passage through calcium chloride or phosphorus pentoxide.

Nitric oxide may also be obtained in the following ways:

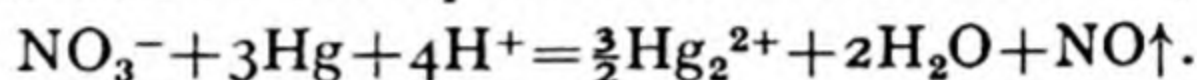
(i) By heating concentrated ferrous sulphate solution with potassium nitrate (or nitric acid) and dilute sulphuric acid:



(ii) By the action of sulphuric acid, diluted with its own volume of water, upon a concentrated solution of potassium iodide and sodium nitrite:

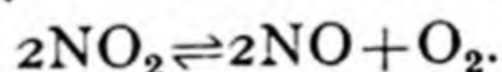


(iii) Small volumes of pure, dry nitric oxide may conveniently be prepared by Lunge's method: concentrated sulphuric acid containing some dissolved nitrate (or nitric acid) is shaken with mercury, when the pure gas is liberated. This reaction is used to estimate nitric acid in the 'spent acids' from nitration processes.



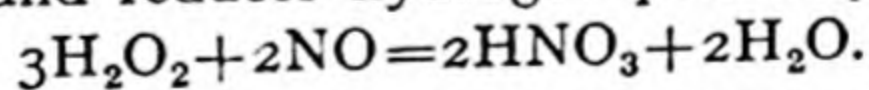
Properties. Nitric oxide is a colourless gas which can be condensed to a colourless liquid, B.P. -152° , and solidified to a colourless solid, M.P. -164° . It is slightly denser than air, and is sparingly soluble in water, 1 c.c. of which dissolves 0.074 c.c. of the gas at 0° .

On exposure to free oxygen, as in the air, nitric oxide is spontaneously oxidized at room temperature to the brown gas nitrogen dioxide, NO_2 : above 140° the reaction is increasingly reversed:

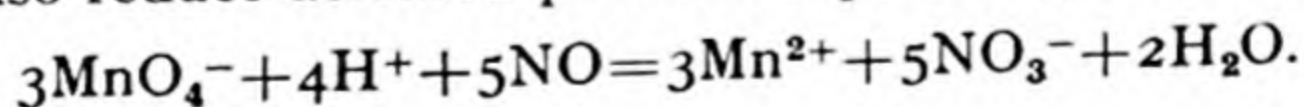


Nitric oxide will not burn, and will support combustion only if the burning body is hot enough (about $1,000^\circ$) to decompose it into nitrogen and oxygen. Like nitrous oxide, it is endothermic, its heat of formation being 21.6 kcal. A mixture of nitric oxide and carbon disulphide vapour burns with a beautiful blue flash if ignited.

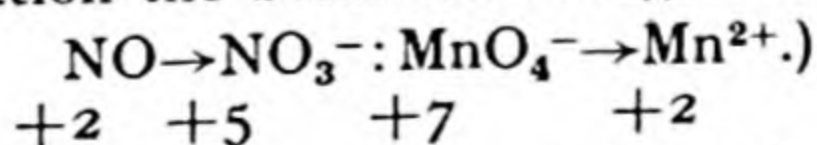
Nitric oxide is fairly reactive. Thus it combines directly with chlorine and bromine, to form *nitrosyl chloride*, NOCl , and *nitrosyl bromide*, NOBr , and reduces hydrogen peroxide to water:



It will also reduce acidified potassium permanganate solution:

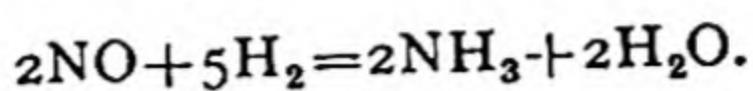


(Note in this equation the balanced changes of oxidation number:



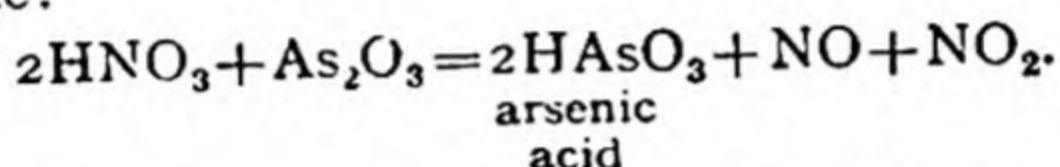
Nitric oxide is reduced to ammonia if passed with hydrogen over

a heated metallic catalyst (reduced nickel, palladium black, platinum black):



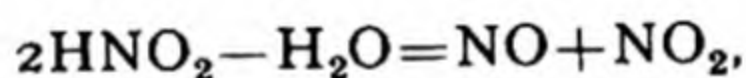
Constitution. If nickel or copper is heated in a measured volume of nitric oxide, the oxide of the metal is formed and nitrogen is left. The volume of nitrogen is half the volume of the original nitric oxide, hence the molecule is NO_x . Since the vapour density is 15, $x=1$.

Nitrous anhydride, dinitrogen trioxide, N_2O_3 , exists in the liquid and solid phases; the gaseous phase consists, at 25° and 760 mm., of about 10 per cent of N_2O_3 molecules, the remainder being a mixture of nitric oxide and nitrogen dioxide. This mixture, known as 'nitrous fumes,' can be obtained by mixing NO_2 and NO in equal volumes, or by the action of concentrated nitric acid on arsenious oxide:

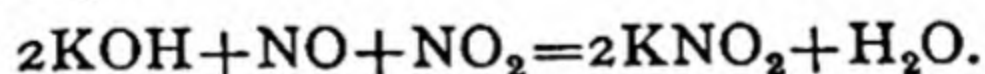


On cooling, both nitrous anhydride and the dioxide liquefy, while the nitric oxide does not. Hence it is not known whether the deep blue colour of the liquid is due to dissolved dioxide, or is really the colour of the nitrous anhydride.

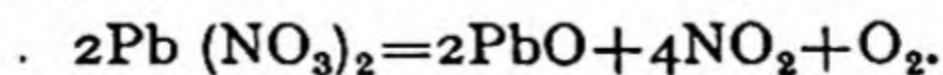
'Nitrous fumes' may be regarded as the anhydride of nitrous acid:



but when passed into water they yield a solution containing both nitrous and nitric acids. The reason is clear: as explained on p. 445, nitrous acid rapidly yields nitric acid in solution, and since the absorption of nitrous fumes by water is fairly slow, time is allowed for this change to take place. However, the nitrous fumes are very rapidly and completely absorbed by concentrated aqueous alkalis, and here only nitrite is formed—as was shown by Gay-Lussac as long ago as 1805:

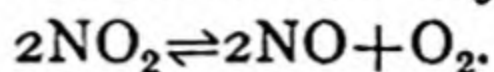


Nitrogen dioxide, NO_2 , is the most familiar oxide of nitrogen, owing to its characteristic brown colour and to the frequency with which it is liberated during experiments with nitric acid. The usual laboratory preparation is to heat lead nitrate crystals:



The mixture of nitrogen dioxide and oxygen is passed through a U-tube surrounded by a freezing-mixture, when the nitrogen dioxide condenses to a yellow liquid. Every one who has carried out this

preparation must have noticed that, very often, the liquid collected is green. This happens when the heating has been too rapid. At the temperature at which lead nitrate decomposes, nitrogen dioxide is largely split up into nitric oxide and oxygen:



When the stream of gas is too rapid, only part of the nitric oxide is re-oxidized in the apparatus, hence the liquid is coloured blue for the reasons explained on p. 443.

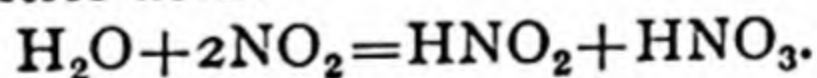
Nitrogen dioxide is formed in torrents when concentrated nitric acid is heated with sugar or starch (which are oxidized to oxalic acid). It is also produced when concentrated nitric acid dissolves copper, an action commonly but doubtfully represented by the equation:



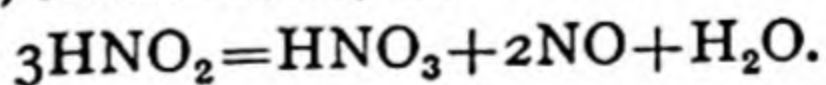
Properties. Nitrogen dioxide is a reddish-brown gas, which on cooling condenses to a yellow liquid, B.P. 21° . At lower temperatures, the liquid freezes to a colourless crystalline solid, M.P. -10° . Vapour density determinations show that, at the boiling-point of the liquid, the vapour consists almost entirely of the double molecules N_2O_4 , dinitrogen tetroxide. With rise of temperature, dissociation into single molecules takes place, and the colour of the gas darkens. At 50° , the equilibrium mixture contains about 40 per cent of NO_2 , at 100° about 90 per cent, and at 140° , 100 per cent. Above 140° , the further dissociation $2\text{NO}_2 \rightleftharpoons 2\text{NO} + \text{O}_2$ begins, and the gas gradually loses its colour. The dissociation into nitric oxide and oxygen is complete at 620° .

Nitrogen dioxide is a very poisonous gas, and care should be taken not to inhale it. Like the other oxides of nitrogen, it will support the combustion of those combustible bodies which are hot enough to decompose it into its elements. Potassium ignites spontaneously in nitrogen dioxide, reducing it to nitric oxide and nitrogen.

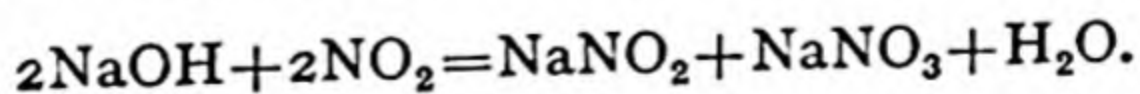
When passed into cold water, nitrogen dioxide yields a mixture of nitrous acid and nitric acid:



On standing, and more readily on warming, the nitrous acid splits up into nitric acid, nitric oxide, and water:

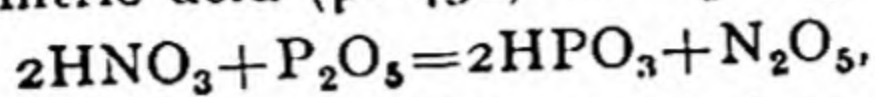


With caustic alkalis, nitrogen dioxide yields a mixture of nitrite and nitrate:

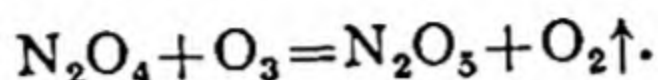


The three reactions above are all examples of *disproportionation* (p. 316).

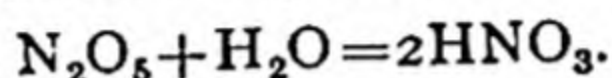
Nitrogen pentoxide, nitric anhydride, N_2O_5 , can be made by distilling fuming nitric acid (p. 452) with phosphorus pentoxide:



and in other ways, e.g. by passing ozone into well-cooled liquid nitrogen dioxide:

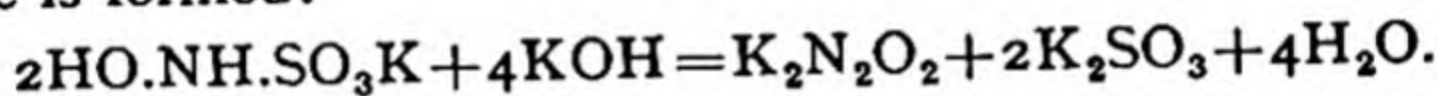


It is a colourless, unstable crystalline solid which melts at 30° to a reddish-brown liquid; this, at 47° , decomposes into nitrogen dioxide and oxygen. Nitrogen pentoxide dissolves in water with a hissing noise, forming nitric acid, of which it is the anhydride:

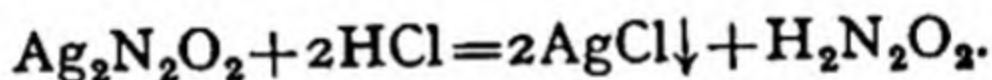


OXYACIDS OF NITROGEN

Hyponitrous acid, $H_2N_2O_2$. When the potassium salt of hydroxylamine sulphonic acid, $HO.NH.SO_3H$, is fused with potassium hydroxide, a mixture of *potassium hyponitrite* and potassium sulphite is formed:

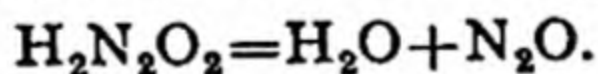


The melt is dissolved in water and neutralized with acetic acid. On adding silver nitrate to the solution, a precipitate of silver hyponitrite is obtained. This is filtered off, washed, carefully dried in a desiccator, and decomposed with an ethereal solution of hydrogen chloride:



The ethereal solution is decanted from the precipitated silver chloride and evaporated in a vacuum. Colourless crystals of hyponitrous acid remain; they are explosive.

Hyponitrous acid dissolves in water, but the solution is unstable and readily decomposes, nitrous oxide being evolved:

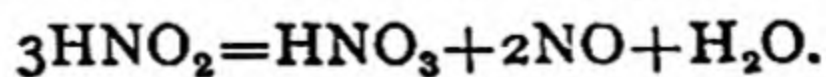


The reaction is irreversible, so that nitrous oxide cannot properly be regarded as hyponitrous anhydride. Hyponitrous acid and the hyponitrites are reducing agents (e.g. towards permanganates). The

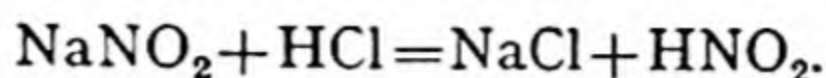
structural formula for the acid is

$$\begin{array}{c} N-OH \\ || \\ HO-N \end{array}$$

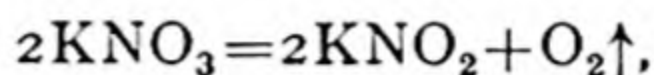
Nitrous acid, HNO_2 . Unlike hyponitrous acid, nitrous acid has not yet been isolated. Even in dilute aqueous solution it rapidly decomposes into nitric acid and nitric oxide:



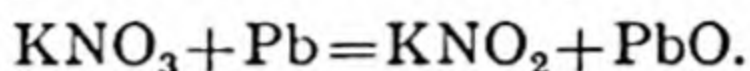
Such a dilute solution, which has a pale blue colour, may be made by adding a dilute acid to a cold solution of sodium or potassium nitrite:



The salts of nitrous acid, *nitrites*, are easily prepared and are much more stable than the acid itself. Nitrites of the alkali metals are obtained by heating the nitrates, either alone:



or with a reducing agent of not too energetic a character, e.g. lead:



See also pp. 299, 443.

Silver nitrite, AgNO_2 , is only slightly soluble in water, and can be precipitated as a yellowish solid by mixing solutions of sodium nitrite and silver nitrate.

Nitrous acid and the nitrites show both oxidizing and reducing powers. Among the *oxidations* they effect (in acid solution) are:

- (i) $\text{H}_2\text{S} + 2\text{HNO}_2 = 2\text{NO} + 2\text{H}_2\text{O} + \text{S}\downarrow.$
- (ii) $\text{NO}_2^- + \text{Fe}^{2+} + 2\text{H}^+ = \text{Fe}^{3+} + \text{H}_2\text{O} + \text{NO}\uparrow.$
- (iii) $\text{NO}_2^- + \text{Fe}(\text{CN})_6^{4-} + 2\text{H}^+ = \text{Fe}(\text{CN})_6^{3-} + \text{H}_2\text{O} + \text{NO}\uparrow.$
- (iv) $\text{NO}_2^- + \text{I}^- + 2\text{H}^+ = \frac{1}{2}\text{I}_2 + \text{H}_2\text{O} + \text{NO}\uparrow.$
- (v) $2\text{NO}_2^- + \text{SO}_3^{2-} + 2\text{H}^+ = \text{SO}_4^{2-} + \text{H}_2\text{O} + 2\text{NO}\uparrow.$

Among the *reductions* are the following:

- (i) $\text{NO}_2^- + \text{I}_2 + 2\text{OH}^- = 2\text{I}^- + \text{H}_2\text{O} + \text{NO}_3^-$ (contrast (iv), above).
- (ii) $5\text{NO}_2^- + 2\text{MnO}_4^- + 6\text{H}^+ = 2\text{Mn}^{2+} + 3\text{H}_2\text{O} + 5\text{NO}_3^-.$

(This reaction can be used in the *estimation* of nitrites, which are, however, better determined by a standard hypochlorite solution, according to the next equation.)

- (iii) $\text{NO}_2^- + \text{ClO}^- = \text{Cl}^- + \text{NO}_3^-$

Constitution of Nitrites. The nitrite ion is $\text{N} \begin{smallmatrix} \diagup \text{O}^- \\ \diagdown \text{O} \end{smallmatrix}$, and the solid salts of nitrous acid are assemblages of metallic cations with these anions, though it is probable that silver nitrite is covalent and of the structure $\text{Ag}-\text{N}^+ \begin{smallmatrix} \diagup \text{O}^- \\ \diagdown \text{O} \end{smallmatrix}$. This view, supported by X-ray analysis of crystalline silver nitrite, would be related to the fact that when silver

nitrite is heated with ethyl iodide the main product is *nitro-ethane*,

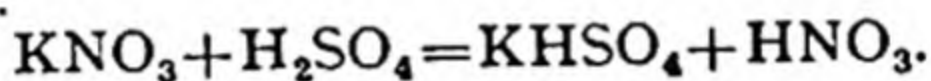
$\text{C}_2\text{H}_5-\text{N}^+\begin{array}{c} \text{O}^- \\ \parallel \\ \text{O} \end{array}$, while potassium nitrite with ethyl iodide yields *ethyl nitrite*, $\text{C}_2\text{H}_5\cdot\text{O}\cdot\text{N}:\text{O}$.

Tests for Nitrites. (i) A solution of a nitrite with ferrous sulphate and *dilute* sulphuric acid gives a brown colour due to the formation of $\text{FeSO}_4\cdot\text{NO}$ (p. 441). Nitrates give the 'brown ring' of this substance only with *concentrated* sulphuric acid.

(ii) Metaphenylene diamine, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, gives a yellow colour when added to an acidified solution of a nitrite.

(iii) *Traces* of nitrites may be detected by addition of sulphanilic acid solution and α -naphthylamine solution, when a red colour is produced even by one part of NO_2^- in 5,000,000 of water.

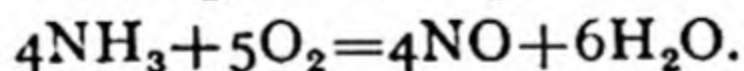
Nitric acid, HNO_3 . Like ammonia, sulphuric acid, sodium carbonate, and many other compounds, nitric acid is manufactured on so large a scale, and is consequently so cheap, that occasion seldom demands its preparation in the laboratory. It can, however, be prepared by distilling concentrated sulphuric acid and potassium or sodium nitrate:



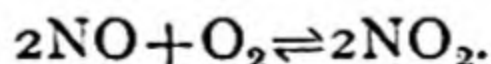
The further reaction, $\text{KHSO}_4 + \text{KNO}_3 = \text{K}_2\text{SO}_4 + \text{HNO}_3$, requires so high a temperature that much of the nitric acid is decomposed.

The distillate of nitric acid is yellow in colour, owing to dissolved nitrogen dioxide; this can be blown out with a current of dry air.

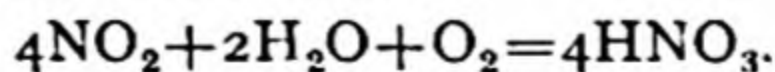
(i) *Manufacture of Nitric Acid from Ammonia.* The success of synthetic methods of manufacturing ammonia has led to a revolution in the manufacture of nitric acid, the bulk of which is now obtained by the catalytic oxidation of synthetic ammonia. At a fairly high temperature (800°), in the presence of a catalyst, e.g. smooth platinum, ammonia is readily oxidized by air, forming nitric oxide, NO , according to the equation:



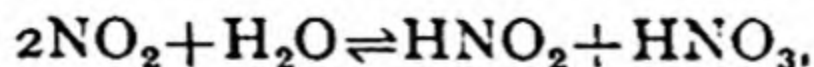
The action is exothermic. If now the nitric oxide is cooled to about 150° , it will combine rapidly with free oxygen (as in the air), forming nitrogen dioxide:



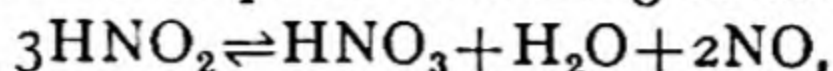
When nitrogen dioxide is dissolved in water in the presence of oxygen, it finally forms nitric acid:



Actually, nitrous acid and nitric acid are first obtained:



but the nitrous acid decomposes according to the equation:

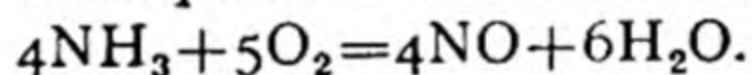


and the nitric oxide is re-oxidized by the excess of air to form nitrogen dioxide, which then undergoes further cycles of the same changes. By suitably designing the absorption apparatus, practically all the nitrogen dioxide can be thus converted into nitric acid.

The details of the process are roughly as follows: Hot ammonia gas, over 99 per cent pure, is mixed with about nine times its volume of dust-free hot air, and the mixture is blown by a steam turbine-blower, A, into the chamber, B (Fig. 81). This chamber (which is about 3 feet in diameter and 8 feet high) consists of an upper and a lower half, united by flanged joints. It can be opened, so that the platinum gauze of approximately 1 mm. mesh, which acts as the catalyst, may be stretched across. The chamber itself is made of cast-iron, and is lined with fire-brick; in section it is circular. To start the action, a sparking-plug is used, just above the platinum gauze. On passing a spark, the hot mixture of ammonia and air at once reacts, as may be seen through a mica window in the side of the chamber.

As mentioned above, the reaction is exothermic, and the platinum becomes red hot. In this state it catalyses the oxidation continuously, so that, once the action has begun, further sparking is unnecessary.

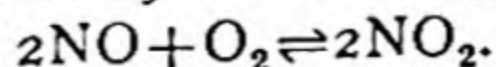
The reaction that takes place in the chamber, B, is therefore:



The mixture of nitric oxide, steam, and nitrogen (from the air) leaves the catalyst chamber at about 800°. It is next passed into a heat-interchanger, C, which consists of a number of pipes in a boiler containing water. The heat of the gases boils the water and produces steam at a high pressure—about 250 lb. per square inch. This high-pressure steam is used for working the steam turbine-blowers and for running generators, etc.

By the time the gases emerge from the heat-interchanger they have become cooled to 300°, but this is still too high a temperature to allow the nitric oxide to combine quickly or at all completely with oxygen, to form nitrogen dioxide; hence a further cooling is necessary. The nitric oxide, nitrogen, and steam are next passed into the first cooler, D, consisting of a spiral tube over which cold water is sprayed, and when they leave it they are mixed with air driven in by another turbine-blower, E.

In the 'oxidizing cooler,' F, the mixed gases are cooled to 150°, at which temperature the nitric oxide reacts satisfactorily with the oxygen of the air blown in by E, forming nitrogen dioxide:



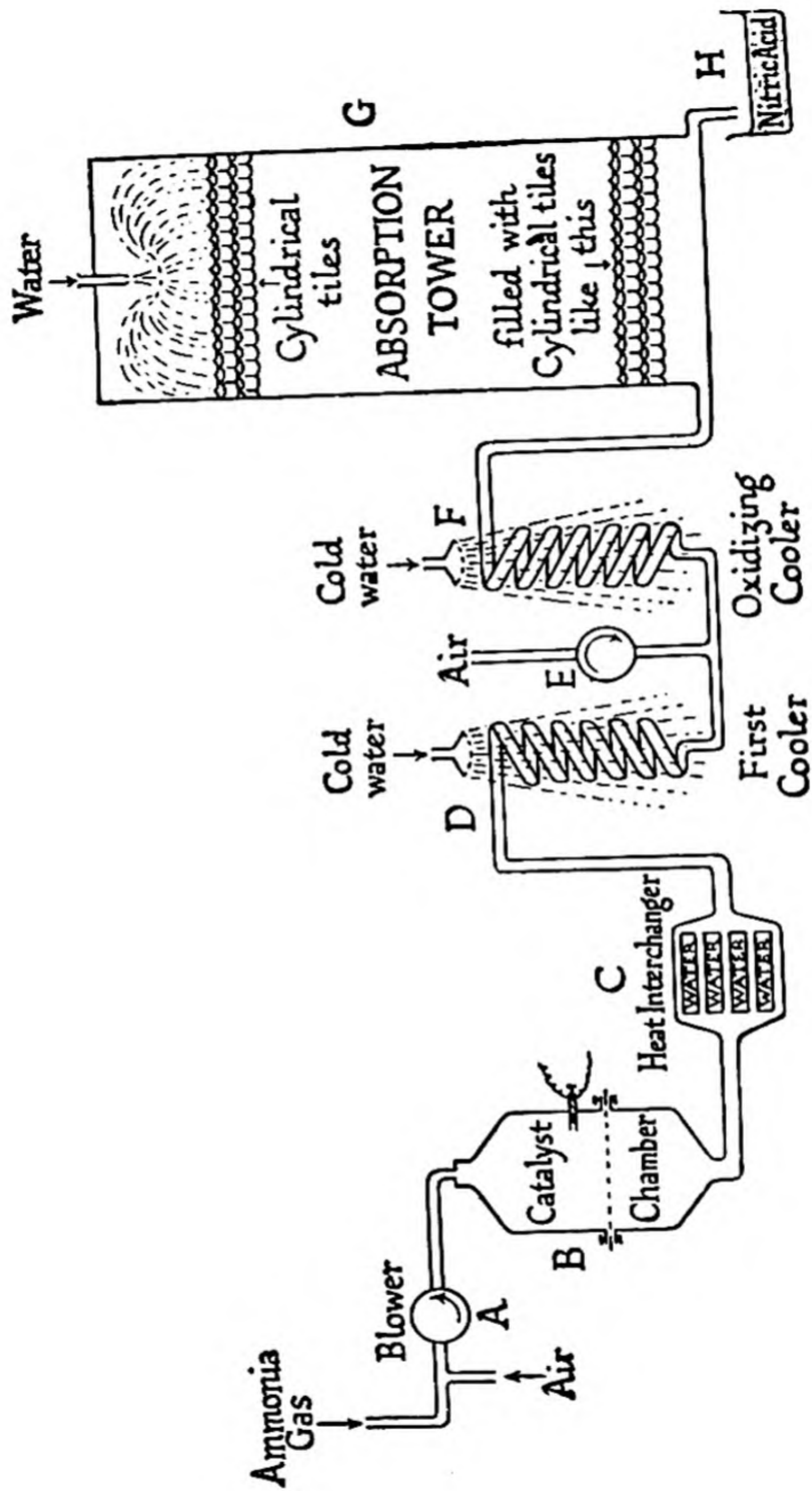
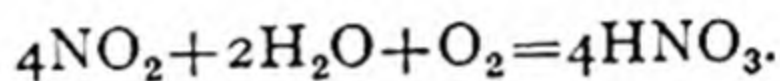


FIG. 81. CATALYTIC PREPARATION OF NITRIC ACID

Unlike nitric oxide, nitrogen dioxide is a very corrosive gas, so that, instead of using cast-iron apparatus, as is used up to this point, the oxidizing cooler and the remaining parts of the plant must be made of some material that is unaffected by nitrogen dioxide. In practice, it is found that a stainless steel, made of iron, nickel, chromium, and tungsten in the proportion of 73 Fe, 18 Ni, 8 Cr, and 1 W, is the best material to employ; this alloy is known by the trade name of 'staybrite'—an infelicitous word perhaps intended to be concisely descriptive.

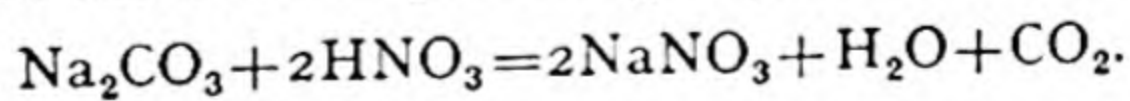
From the oxidizing cooler, F, the gases (now consisting of nitrogen dioxide, nitrogen and oxygen from the air, and steam) pass into the large absorption tower, G, which also is made of stainless steel and is about 50 feet high and 25 feet in diameter. This tower is packed with short cylindrical tiles, made of an acid-resisting material. At the top, a jet of distilled water is directed forcibly downwards on a kind of perforated saucer, which causes a spray to be distributed regularly over the top of the tiles. The water then trickles down through the tiles, where it meets the ascending nitrogen dioxide, nitrogen, and oxygen; the steam is, of course, condensed.

In the absorption tower the nitrogen dioxide reacts with the water and the extra oxygen from the air blown in at E, forming nitric acid according to the equations given above, the net result being:

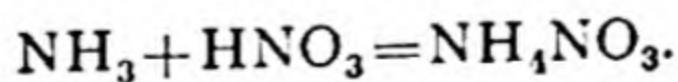


Since an excess of water is used, the acid produced is somewhat dilute; 45 per cent is the usual working figure. This acid is run out from the bottom of the tower into the tank, H. The absorption tower has to be large, partly on account of the large quantity of gases to be treated (about 6,000 cubic metres per hour), and partly because the action $2\text{NO} + \text{O}_2 \rightleftharpoons 2\text{NO}_2$ is rather slow.

If concentrated nitric acid is required, the dilute acid is mixed with concentrated sulphuric acid and the mixture distilled; concentrated nitric acid distils over and dilute sulphuric acid is left in the still. This acid is then concentrated (p. 533) and used again. For many purposes, however, dilute nitric acid is quite suitable. Thus sodium nitrate is made from it by neutralization with sodium carbonate from the SOLVAY process (p. 293):

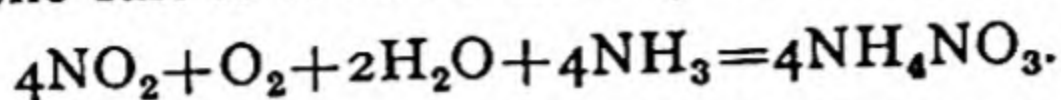


A good deal of the acid is converted into ammonium nitrate, NH_4NO_3 , by neutralization with ammonia solution:



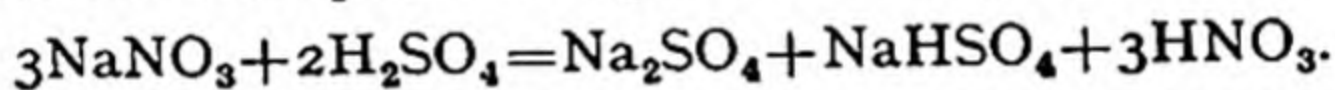
Alternatively ammonium nitrate is obtained by blowing a mixture

of air and ammonia gas into the gases emerging from the oxidizing cooler, when the salt is formed directly as a crystalline powder:



Ammonium nitrate is an excellent artificial manure, but is deliquescent and therefore troublesome to store and transport. This difficulty is overcome by mixing it with chalk (calcium carbonate, CaCO_3). The finely ground chalk is mixed with a concentrated solution of ammonium nitrate, until the mixture forms a semi-liquid paste. This paste is then sprayed from the top of a high tower, and by the time it reaches the ground it has assumed the form of roundish solid pellets. The pellets are sold as a fertilizer under the name of 'nitro-chalk.'

(ii) *Manufacture of Nitric Acid from Sodium Nitrate.* Practically the whole of the commercial output of nitric acid was formerly obtained by a large-scale modification of the usual laboratory preparation, viz. the action of concentrated sulphuric acid upon a nitrate. The method is still employed to some extent. A charge of one or two tons of sodium nitrate (Chile saltpetre) is heated with approximately the same weight of concentrated sulphuric acid in cast-iron retorts, the temperature being adjusted so that the reaction proceeds beyond the formation of the bisulphate and gives a residue of sulphate and bisulphate in equimolecular proportions:



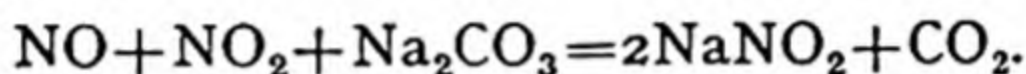
Most of the nitric acid vapour is condensed in water-cooled condensing-pipes made of earthenware, glass, silica, or other resistant material. Any uncondensed vapour passes into towers packed with earthenware balls; here it is absorbed in a stream of water which trickles down over the balls.

The residue of sodium bisulphate and sulphate is known as 'nitre-cake.'

(iii) *Manufacture of Nitric Acid from the Air.* A third method of manufacturing nitric acid, which at one time appeared to have very rosy prospects but which has been rendered obsolete or at least obsolescent by the ammonia-oxidation method, was invented by the Norwegian chemical engineers BIRKELAND and EYDE at the beginning of the present century. It consists essentially in blowing air through an electric arc spread out into a thin disk, some 6 feet in diameter, by means of a powerful electromagnetic field. Under these conditions the endothermic reaction $\text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO}$ takes place, the proportion of nitric oxide in the equilibrium mixture being, however, very small—3 or 4 per cent—even at the high temperature of the arc. If the mixture of gases emerging from the flame were allowed to cool slowly, practically all the nitric oxide

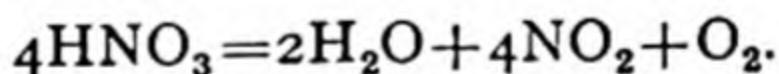
would decompose again; for, since it is an endothermic compound, the proportion of it in the equilibrium mixture decreases as the temperature falls (LE CHATELIER'S principle). By cooling the gases quickly, however, the rate at which the nitric oxide decomposes is so greatly lowered that the equilibrium has not sufficient time to re-establish itself completely; and below $1,000^{\circ}$ the rate of decomposition becomes inappreciably small.

The gases leaving the furnace are therefore cooled as rapidly as possible to $1,000^{\circ}$ by passing through heat-interchangers, and are subsequently further cooled to about 150° to allow the formation of nitrogen dioxide (cf. p. 442). This is then absorbed in water, when nitric acid is produced. In order to remove any residual oxides of nitrogen, the gases are next passed into a tower down which a solution of sodium carbonate flows; here the absorption is complete and a solution of sodium nitrite (with a little sodium nitrate) is obtained:



The arc process was worked principally in Norway (Notodden, etc.) and a few other countries where electrical energy can be generated at low cost from water-power. Much of the Norwegian acid was converted into basic calcium nitrate (normal calcium nitrate is deliquescent) for use as a fertilizer ('Norwegian saltpetre' or 'air-saltpetre').

Properties of Nitric Acid. Nitric acid—the *aqua fortis*, or 'strong water,' of the alchemists and pharmacists—is a fuming, colourless, oily liquid (specific gravity 1.52) which freezes to a white crystalline solid at -41° . The pure liquid is unstable, and on standing undergoes partial decomposition:



The decomposition is accelerated at the boiling-point of the acid (86°). In a full, unopened bottle of concentrated nitric acid the acid does not turn yellow when exposed to light; but light soon decomposes the *vapour* of the acid, and the brown fumes so produced dissolve in the liquid and colour it yellow.

The 'concentrated nitric acid' of the reagent shelves is the constant-boiling mixture (B.P. 121°); it contains 68 per cent of HNO_3 , and has a density of 1.41 gm. per c.c. By distillation of this solution with concentrated sulphuric acid, 'fuming nitric acid' of about 98 per cent strength may be obtained.

The concentrated acid is a violent corrosive poison, and rapidly destroys flesh and other organic matter.

The chemical properties of nitric acid can best be understood by noticing that it can act in *three* main ways, viz. (a) as a strong acid,

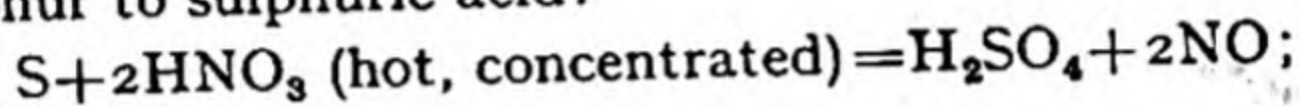
(b) as a powerful oxidizing agent, and (c) as a nitrating agent. The very concentrated acid is but little ionized, and behaves rather as HO.NO_2 than as $[\text{H}^+][\text{NO}_3^-]$.

(a) *Acid Properties.* Nitric acid shows the usual properties of strong acids. It is highly ionized in aqueous solution, and its salts with strong bases yield neutral solutions in water. However, in solution in absolute alcohol it behaves as a *weak* acid.

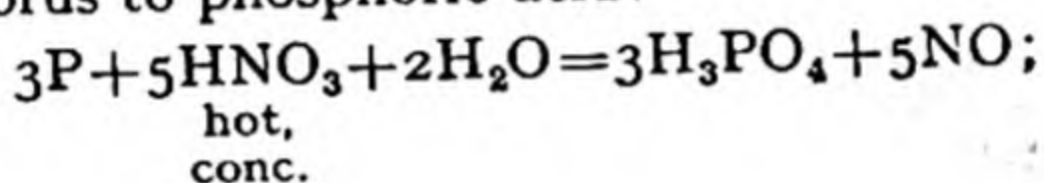
(b) *Oxidizing Properties.* Nitric acid is a comparatively unstable compound and contains nearly 80 per cent by weight of oxygen; it has very great powers of oxidation, and is easily reduced to NO_2 , ' N_2O_3 ', NO , N_2O , N_2 , NH_2OH (hydroxylamine), and even NH_3 . The stage to which the reduction of the acid proceeds is dependent on various factors, e.g. temperature, concentration of the acid, and the nature of the substance oxidized.

Under suitable conditions nitric acid will oxidize:

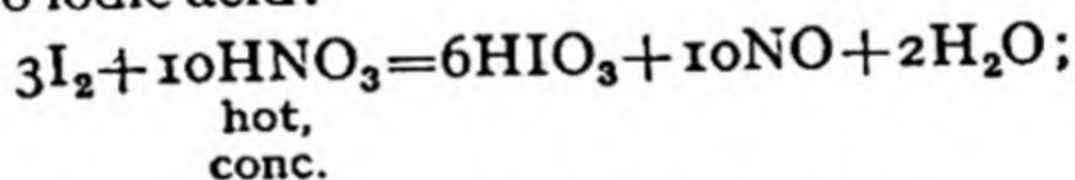
(i) sulphur to sulphuric acid:



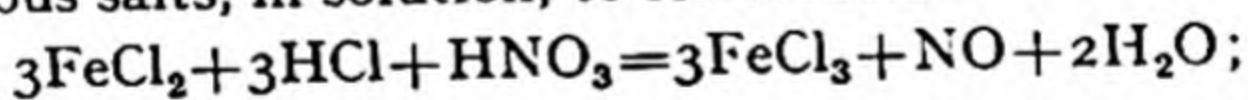
(ii) phosphorus to phosphoric acid:



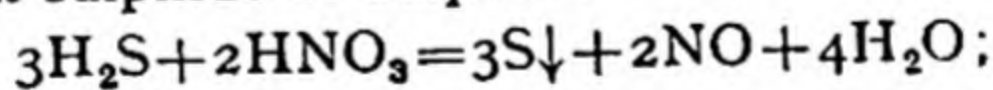
(iii) iodine to iodic acid:



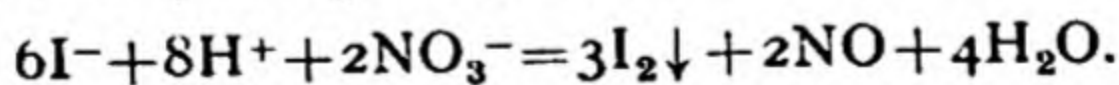
(iv) ferrous salts, in solution, to ferric salts:



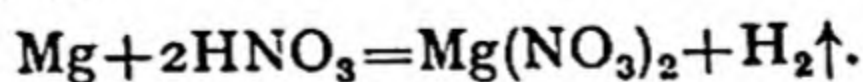
(v) hydrogen sulphide to sulphur:



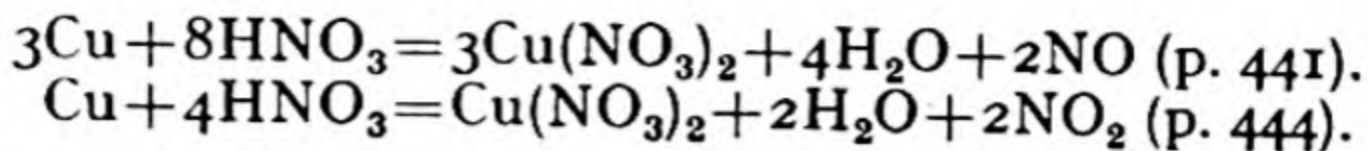
(vi) iodine ions (as in potassium iodide solution) to iodine:



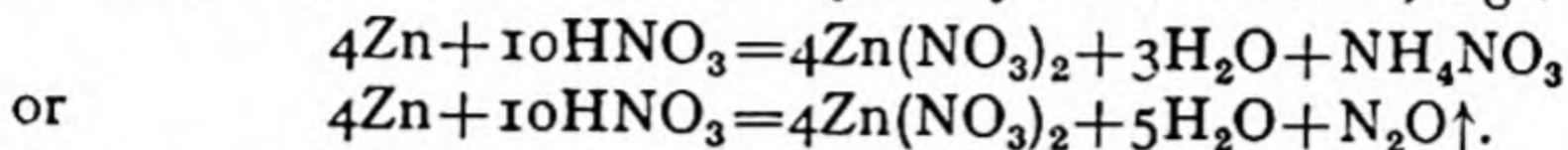
Nitric acid under ordinary conditions readily attacks most metals. If very dilute, it reacts with manganese and magnesium to yield the corresponding nitrates and *gaseous hydrogen*—a very unusual occurrence, since as a rule it gives only the oxidation product of hydrogen, viz. water:



More typical are the reactions:

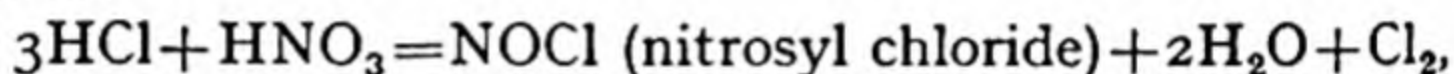


With zinc, dilute nitric acid yields nitrous oxide and ammonium nitrate, together with some hydroxylamine nitrate, e.g.:



Tin, on the other hand, is converted into a hydrated stannic oxide by concentrated nitric acid. This reaction is described on p. 413. Iron, chromium, nickel, and certain other metals are rendered 'passive' (p. 246) by the concentrated acid. If the traces of nitrous acid present in ordinary nitric acid are removed by the addition of urea, nitric acid attacks copper and some other metals only with extreme slowness.

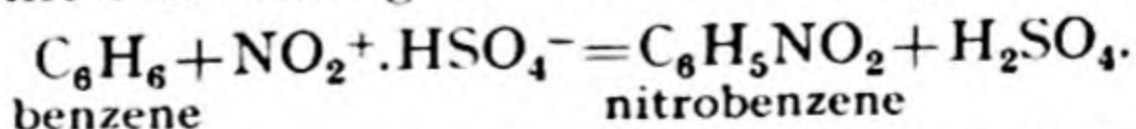
A mixture of concentrated nitric acid and concentrated hydrochloric acid is known as *aqua regia*, or 'royal water.' It contains free chlorine:



and is therefore able to dissolve gold and platinum as their chlorides, AuCl_3 and PtCl_4 . It also attacks silver, but does not dissolve it, since silver chloride is insoluble.

Nitric acid will often effect drastic oxidation of organic compounds, particularly aliphatic. Thus it oxidizes sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, to oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$, and warm sawdust to carbon dioxide and water. When, as is usually the case, it contains traces of nitrous acid, it oxidizes ethyl alcohol explosively.

(c) *Nitrating Properties.* The substitution of one or more $-\text{NO}_2$ groups for the same number of hydrogen atoms in the molecule of an organic (generally aromatic) molecule is described as *nitration* and the products are called *nitro-compounds*. The nitration of a hydrocarbon, such as benzene, is carried out by treating it with 'nitrating acid,' which is a mixture of concentrated nitric and concentrated sulphuric acids: in nitrating more reactive compounds anhydrous acetic acid may be substituted for sulphuric acid. Not only is the oxidizing power of nitric acid much moderated in such mixtures but they contain a cation NO_2^+ ($\text{O}=\overset{+}{\text{N}}=\text{O}$) which is now thought to be the essential agent of nitration, e.g. for benzene:

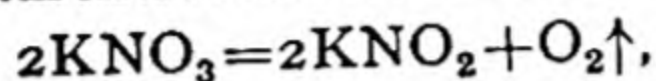


It will be noted that the *nitronium* cation, NO_2^+ , is isoelectronic with carbon dioxide, $\text{O}=\text{C}=\text{O}$.

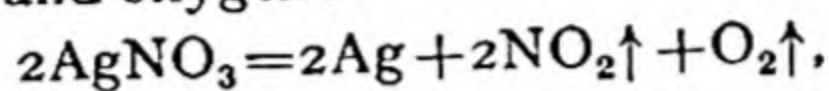
N.B. The so-called 'nitration' of glycerol is not nitration but

esterification. The product is not a nitro-compound but glyceryl trinitrate.

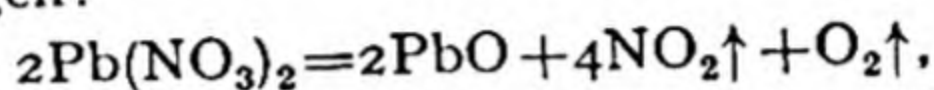
Nitrates. The metallic nitrates are all soluble in water, and like the acid itself are powerful oxidizing agents. They decompose on heating, the alkali-metal nitrates into the nitrite and oxygen:



the nitrates of heavier metals with unstable oxides into metal, nitrogen dioxide, and oxygen:

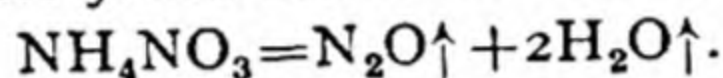


the anhydrous nitrates of other metals into metallic oxide, nitrogen dioxide, and oxygen:



and hydrated nitrates into metallic oxide, nitric acid vapour, steam, oxides of nitrogen, and oxygen.

Ammonium nitrate yields nitrous oxide and steam when heated:



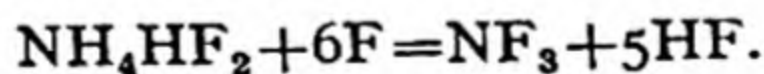
Tests for Nitrates. (i) The 'brown-ring' test for a nitrate depends upon the reduction of the nitrate to nitric oxide by the ferrous sulphate, some of which then combines with the nitric oxide to form the brown compound $\text{FeSO}_4\cdot\text{NO}$ (p. 441).

(ii) With brucine and concentrated sulphuric acid, a solution of a nitrate gives a fine red colour.

(iii) When heated with sodium hydroxide solution and DEVARDA'S alloy (Cu 50, Al 45, Zn 5 per cent), nitrates are quantitatively reduced to ammonia. This reaction may be used in the *estimation* of nitrates.

NITROGEN HALIDES

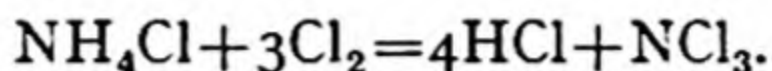
Nitrogen fluorides. Nitrogen trifluoride, NF_3 , may be prepared by the electrolysis of fused ammonium hydrogen fluoride, NH_4HF_2 , or by treating ammonia with fluorine. In the former reaction, fluorine liberated at the anode attacks some of the ammonium hydrogen fluoride as follows:



Nitrogen trifluoride is a colourless gas, which can be condensed on cooling to a colourless, mobile liquid boiling at -129° and freezing at -217° . Unlike nitrogen chloride and iodide (q.v.), nitrogen trifluoride is a very stable substance with a heat of formation of -26 kcal. It is insoluble in water and alkalis, and does not react with hydrogen unless the mixture is sparked, when a violent action takes place and nitrogen and hydrogen fluoride are obtained.

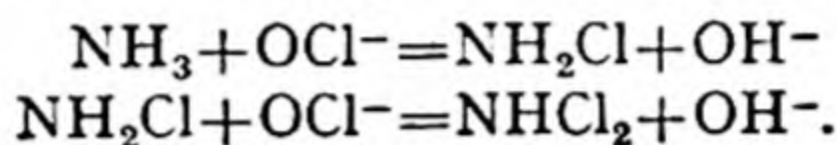
The gaseous fluorides NHF_2 and NH_2F are also known, as well as gaseous compounds believed to be NF_2 and N_2F_2 .

Nitrogen trichloride, NCl_3 , can be prepared (CAUTION: DO NOT TRY THIS!) by passing chlorine into warm (35°) concentrated ammonium chloride solution:

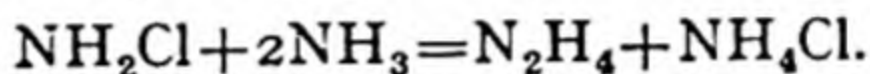


It is a volatile yellow oil, which explodes with great violence when exposed to sunlight, when brought into contact with easily oxidized organic matter, when heated, or often when merely prodded with a needle.

The chlorides NH_2Cl and NHCl_2 may be obtained in aqueous solution by the interaction of aqueous ammonia with hypochlorites:



Mono-chloramine, NH_2Cl , with excess of ammonia (in the presence of protective colloids, p. 265) gives hydrazine (p. 437):



Nitrogen bromides, NH_2Br and NHBr_2 , have been obtained in ethereal solution by passing ammonia into an ethereal solution of bromine.

Nitrogen iodides. The black explosive powder made by pouring 0.880 ammonia on to powdered iodine is the complex $\text{NI}_3 \cdot \text{NH}_3$.

THE NITROGEN CYCLE

Nitrogen is a constituent element of protoplasm, proteins, and other substances present in living organisms. Animals obtain their nitrogen by consuming proteins, etc., ultimately synthesized by plants from atmospheric carbon dioxide and the soil water, which contains simple nitrogenous compounds such as nitrates. Animals are incapable of effecting this synthesis, so that all forms of animal life—including man—are dependent upon plant life.

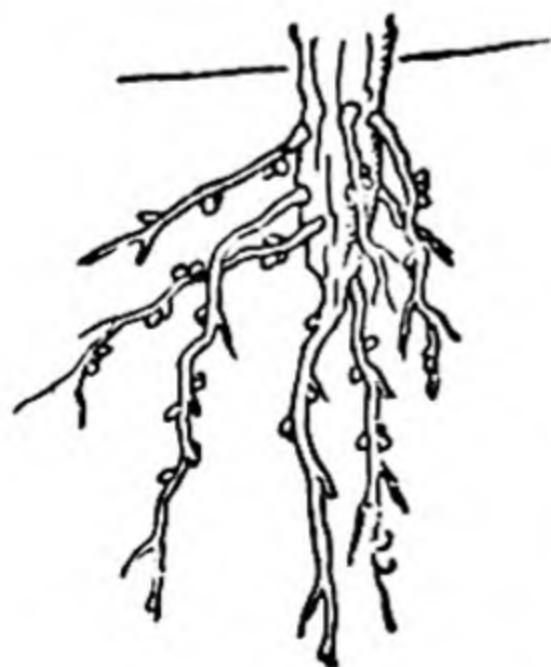


FIG. 82. NODULES ON ROOTS OF A LEGUMINOUS PLANT

Ordinary fertile soil contains nitrates, which are absorbed in solution by the plant roots, and are used in building up the complex nitrogenous compounds characteristic of life. The supply of nitrates in the soil is, however, replenished naturally in several ways:

(i) During thunderstorms, the flashes of lightning synthesize a certain amount of nitric acid from atmospheric nitrogen, oxygen, and moisture. This is washed down in the rain.

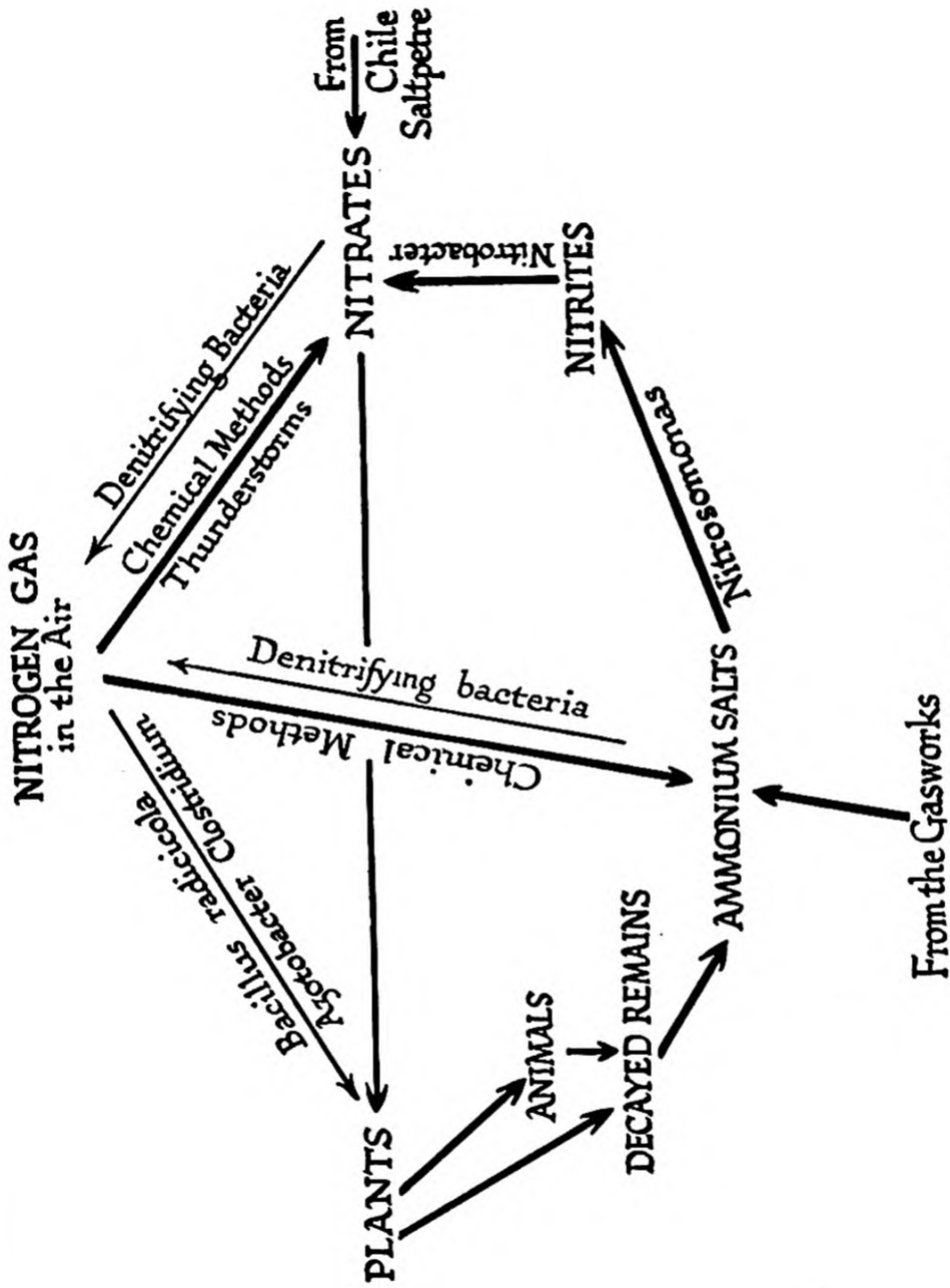


FIG. 83. THE NITROGEN CYCLE

(ii) Certain varieties of bacteria, e.g. *Azotobacter chroococcum* and *Clostridium pasteurianum*, normally present in soil, are able to 'fix' free atmospheric nitrogen, i.e. they can convert it into nitrogenous compounds. Another kind of nitrogen-fixing bacterium is *Bacillus radicicola*; this species attaches itself to the roots of leguminous plants where it forms the characteristic nodules shown in Fig. 82.

(iii) The nitrogenous compounds in animal excreta, and in dead animals and plants, are broken down into ammonia by bacterial action when returned to the soil. In the presence of air the ammonia is oxidized first to nitrites (by the bacterium *Nitrosomonas*) and then to nitrates (by *Nitrobacter*).

Under natural conditions, therefore, a supply of nitrates is maintained in the soil, even though certain other bacteria—'denitrifying bacteria'—decompose nitrites and nitrates with evolution of free nitrogen.

Agriculture and other practices of civilization, however, seriously upset the balance of nature, by the transference of crops from country to country, by the discharge of sewage (which contains nitrogenous compounds) into the sea, and in other ways. Moreover, it rarely happens that unmanured soil contains the optimum content of nitrates, so that, for all these reasons, the application of nitrogenous fertilizers to cultivated soil is a necessity. The natural nitrogen cycle is therefore modified and amplified by man, as indicated diagrammatically on p. 457.

PHOSPHORUS, P

Atomic number: 15. Atomic weight: 30.975. Specific gravity: 1.8 (yellow). Melting-point: 44.1° (yellow). Boiling-point: 287° (yellow).

History. Phosphorus, the 'light-bearer,' so called on account of its characteristic property of glowing in the dark, was discovered by BRAND of Hamburg about 1674. His method was to distil a mixture of concentrated and fermented urine with sand, when the phosphorus



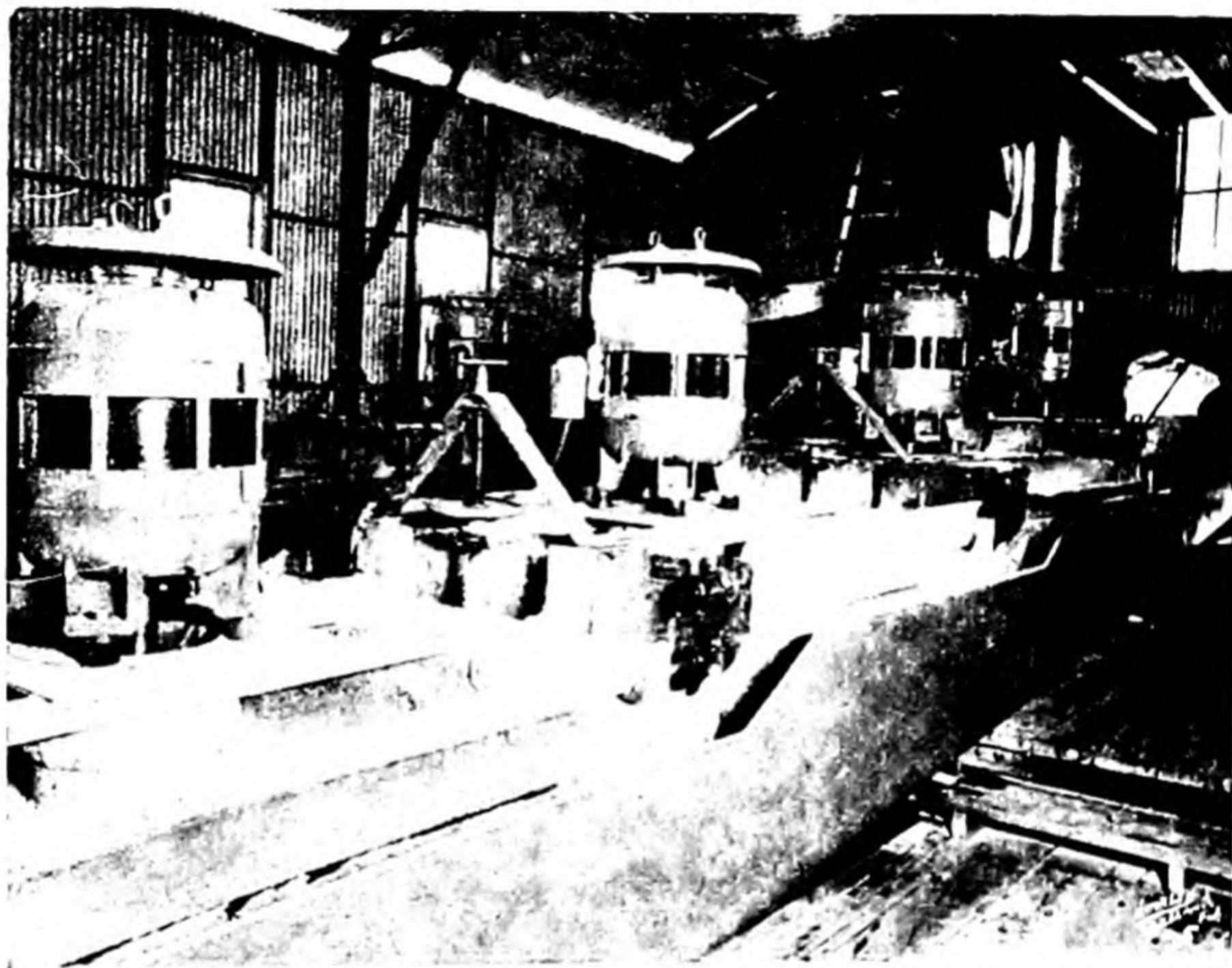
International Agricultural Corporation, Florida

FIG. 84. MINING PHOSPHATE IN FLORIDA

was obtained as a blackish solid. KUNCKEL (1630–1703), an accomplished German chemist, after vainly trying to purchase the secret from Brand (who had, in the meanwhile, already sold it to an adventurer named KRAFFT), hit upon the same method of preparation independently in 1678. Krafft exhibited the element in England, and BOYLE, having received a hint from Krafft, made a third discovery (1680) of its extraction from urine. Boyle published the details of his process, hence for many years phosphorus

was known as 'English phosphorus.' In 1769-70 GAHN discovered that phosphorus is a constituent of bones, an observation confirmed by SCHEELE in 1771, who also described a method of preparing it from bone-ash. LAVOISIER (1772), from a study of its behaviour on combustion, showed that it was probably an element.

Occurrence. Phosphorus is not found free in nature, but *phosphates* are abundant and widely distributed. *Calcium phosphate*



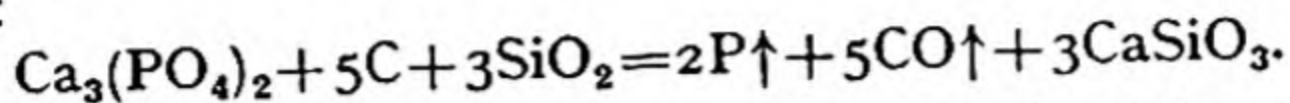
American Agricultural Chemicals Co., Florida

FIG. 85. FLOTATION CELLS FOR CONCENTRATING PHOSPHATE ROCK

$\text{Ca}_3(\text{PO}_4)_2$ —otherwise *rock-phosphate* or *phosphorite*—occurs in large deposits in the United States (Florida, Tennessee), North Africa, and other localities; it has been estimated that 1,000,000,000 tons are available in Morocco alone. *Aluminium phosphate*, or *wavellite*, AlPO_4 ; *ferrous phosphate*, or *vivianite*, $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$; and *apatite*, $\text{CaF}_2 \cdot 3\text{Ca}_3(\text{PO}_4)_2$, are also found naturally. Phosphorus is an essential element of protoplasm, the living substance of animals and plants. Bones contain about three-fifths of their weight of calcium phosphate.

Extraction. Rock-phosphate is finely crushed and mixed with

sand and powdered coke or anthracite. The mixture is then heated to $1,400^{\circ}$ – $1,500^{\circ}$ in an electric furnace, when phosphorus vapour comes off:



(It should be noted that the process is electrothermic, not electrolytic.) The calcium silicate forms a fusible slag, which is run off from the furnace as required, while the gases are led into water.

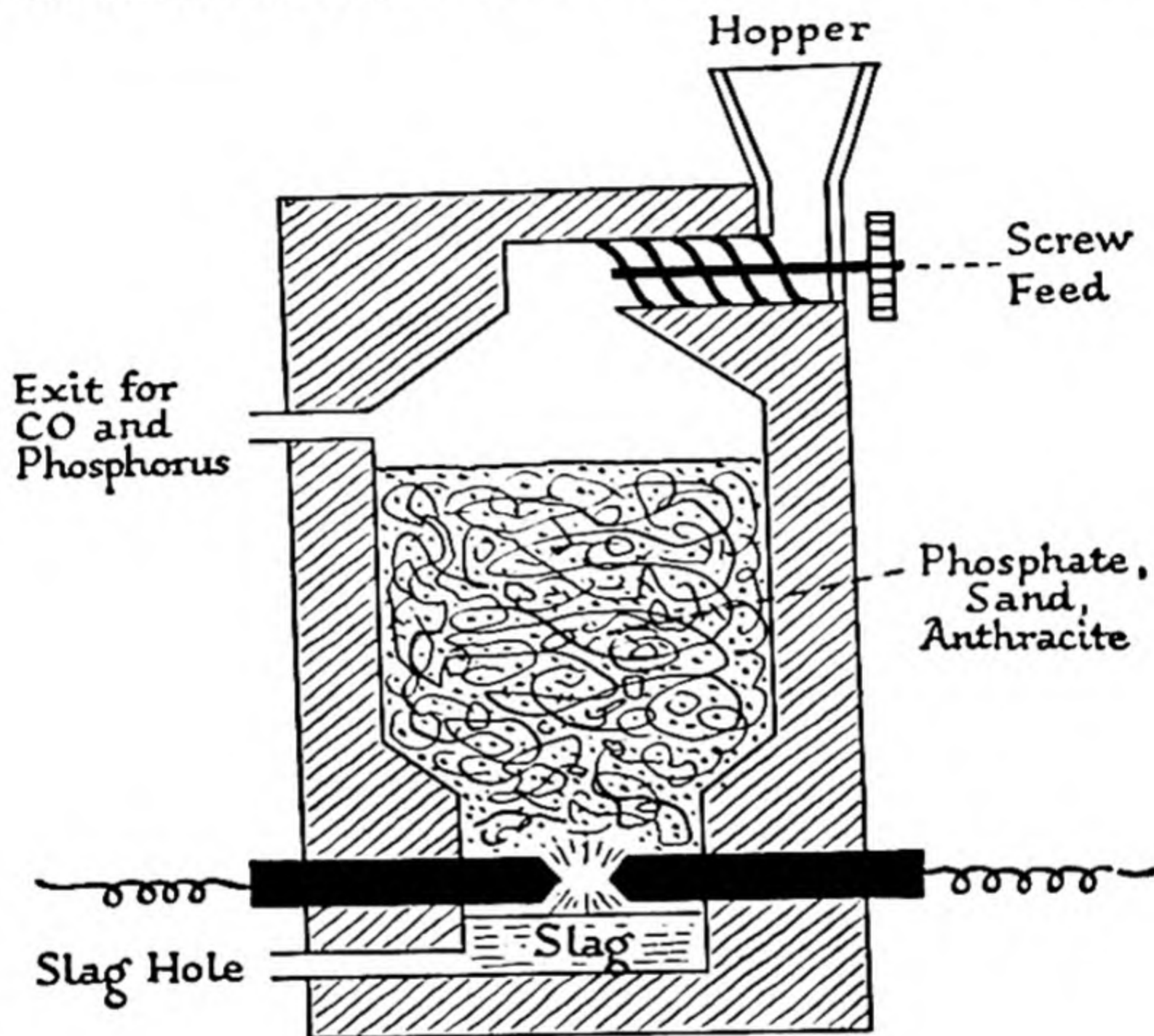


FIG. 86. PHOSPHORUS FURNACE

Here the phosphorus condenses to a dark, impure solid mass of its yellow allotrope (see below), while the carbon monoxide passes on and is collected for use as fuel. Fresh charges of phosphate, sand, and coke are fed in at the top of the furnace through an Archimedean-screw hopper.

The crude phosphorus is purified by melting it under an acidified solution of sodium dichromate which oxidizes some of the impurities to soluble compounds and converts others to a scum which floats to the surface of the solution. After some hours the molten phosphorus is removed, squeezed through canvas bags, and run

into tubular or wedge-shaped moulds, where it solidifies. Owing to the ease with which it inflames, it is preserved under water.

Properties. Phosphorus exists in allotropic modifications, of which the chief are *yellow* (or *white, colourless*) phosphorus and *red* (or 'amorphous') phosphorus.

Yellow phosphorus is a nearly colourless, translucent, wax-like crystalline solid of specific gravity 1.8; it melts at 44.1° and boils at 287° . Up to $1,000^{\circ}$ the density of the vapour corresponds to the molecular structure P_4 ; above this temperature dissociation into diatomic molecules begins. Yellow phosphorus is insoluble in water, but dissolves in many organic solvents such as carbon

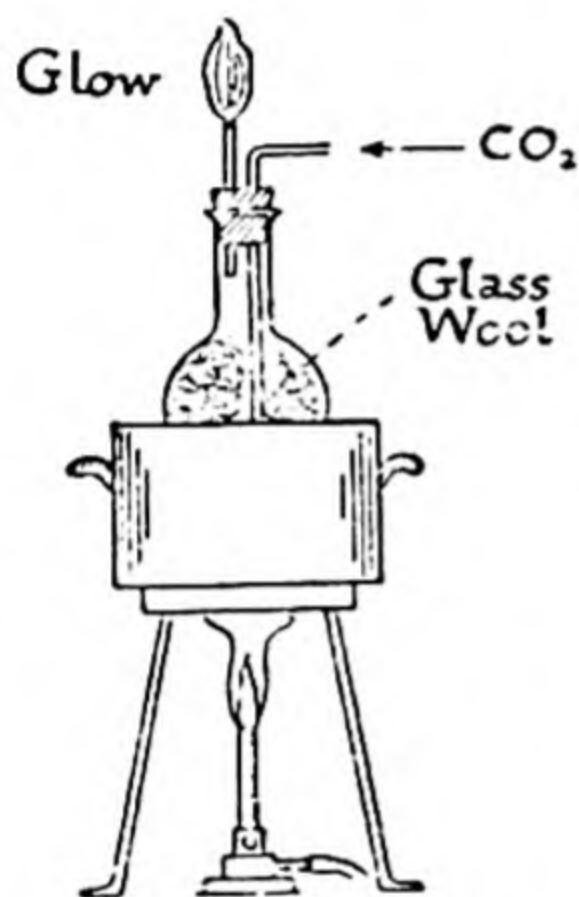


FIG. 87. SMITHELLS'S EXPERIMENT

disulphide, olive oil, and benzene. When prepared in the finely divided state by the rapid evaporation of its solution in carbon disulphide, it spontaneously ignites in the air at ordinary temperatures. Larger pieces take fire if warmed to about 30° in moist air or 50° in dry air.

If exposed to air in the dark, yellow phosphorus emits a ghostly, greenish light. This phenomenon is described as *chemiluminescence*, and is probably caused by the slow oxidation of phosphorus vapour given off from the solid element. The first product (during the formation of which the glow occurs) is *phosphorous oxide*, P_4O_6 . This is subsequently oxidized to *phosphoric oxide*, P_4O_{10} , without further chemiluminescence. The glow of phosphorus is very well seen in SMITHELLS'S experiment. Two or three pieces of yellow phosphorus are placed

in a flask which is then packed with glass wool and heated on a water-bath. A current of carbon dioxide is passed through the flask, and the phosphorus vapour carried by the gas forms a cold, luminous flame when it reaches the air.

Phosphorus is a very reactive element, its combination with the halogens, for example, being accompanied by the evolution of heat and light. It has a great affinity for oxygen and is consequently a reducing agent. With hydrogen, on the other hand, it will not combine directly, though phosphorus hydrides can be made indirectly. Phosphorus combines with many metals to form *phosphides*, e.g. silver phosphide, Ag_3P , and calcium phosphide, Ca_3P_2 ; and with sulphur to form phosphorus sulphides.

Non-oxidizing acids are without effect on phosphorus, but concentrated nitric acid attacks it violently, forming *phosphoric acid*

with liberation of oxides of nitrogen. Hot concentrated sulphuric acid also oxidizes phosphorus to phosphoric acid, being itself reduced to sulphur dioxide.

Red phosphorus. On exposure to light, 'yellow' phosphorus gradually changes from its original translucent white form to the opaque yellowish condition which justifies its common name. Further exposure slowly converts the yellow colour to red, and examination of the red product shows that it is a microcrystalline allotrope, red phosphorus. The change can be accelerated by heating to 240° – 250° , and by the addition of a crystal of iodine as catalyst, but takes some time to go to completion. It would proceed more quickly at higher temperatures, but since it is exothermic (P , yellow = P , red: $\Delta H = -4.4$ kcal.) it becomes difficult to manage in practice if the temperature is above 250° . Remaining traces of the yellow allotrope are removed from the red phosphorus by boiling with caustic soda solution, which reacts with yellow phosphorus forming phosphine (gas) and sodium hypophosphite (soluble) but does not attack red phosphorus.

Red phosphorus has a specific gravity of 2.2, and is therefore considerably denser than yellow phosphorus (1.8). It does not glow in the dark, and is so slowly oxidized in the air that no special precautions are necessary to preserve it. When heated in air it ignites at 250° , i.e. some 200° above the ignition point of yellow phosphorus. It melts at 590° (under pressure) and boils at about 740° ; the vapour on cooling gives crystals of yellow phosphorus. Red phosphorus is insoluble in carbon disulphide, and is not noticeably poisonous; yellow phosphorus is extremely poisonous, and its industrial use is prohibited except under stringently regulated conditions.

The vapour pressure of yellow phosphorus is greater than that of red phosphorus at all temperatures; hence there can be no transition temperature at which the two forms are in equilibrium with one another. The yellow allotrope is said to be *metastable* with regard to the red, into which it gradually passes. The direct reverse change cannot take place, and phosphorus is therefore described as a *monotropic** substance, in contrast to such a substance as sulphur, which is *enantiotropic*,† since there is a definite transition temperature above which rhombic sulphur passes into monoclinic sulphur and below which monoclinic sulphur passes into rhombic sulphur.

Black phosphorus (specific gravity 2.7) is obtained by subjecting yellow phosphorus to great pressure (12,000 atmospheres) at 200° . It is reported to possess a small electrical conductivity. *Violet phosphorus* and *Schenk's scarlet phosphorus* apparently differ

* i.e. moving in one direction.

† i.e. moving in both directions.

from red phosphorus only in the size of their crystals, and are not considered to be distinct allotropes.

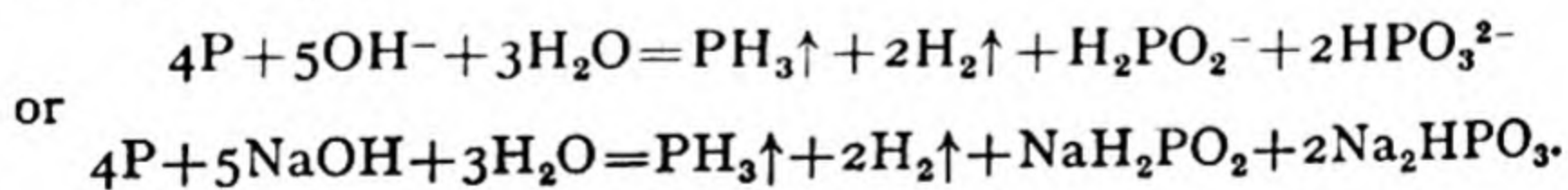
Uses. Phosphorus is used to some extent as a rat poison, but one need not be a lover of these vermin to feel that less inhuman methods of exterminating them are preferable. Of the thirty to forty thousand tons of phosphorus manufactured every year, the great bulk is employed in the match industry. In safety matches the heads are made of a mixture of potassium chlorate, ferric oxide, manganese dioxide, potassium dichromate, and/or other oxidizing agents, together with gum, glue, ground glass, and a little sulphur. The side of the box is coated with a mixture of red phosphorus, antimony sulphide, and gum. When the match-head is rubbed against the prepared surface, the heat produced is sufficient to make the phosphorus actually in contact with the head burn in the oxidizing mixture. The burning phosphorus ignites the sulphur, and this in turn sets fire to the wooden stem.

In 'strike anywhere' matches, the heads are made of a mixture of *tetraphosphorus trisulphide* (or *phosphorus sesquisulphide*), P_4S_3 , potassium chlorate, ground glass, and glue. The heat of friction is sufficient to ignite this mixture.

Phosphorus is also used in making smoke bombs, and as an ingredient of the very tough alloy, *phosphor-bronze*.

COMPOUNDS OF PHOSPHORUS

Phosphine, PH_3 . When yellow phosphorus is boiled with an aqueous solution of caustic alkali, in an apparatus from which all the air has been displaced by an inert gas, e.g. coal-gas, impure phosphine is given off as a spontaneously inflammable gas:



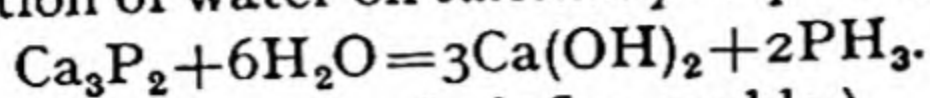
The sodium salts formed are the *hypophosphite*, NaH_2PO_2 , and the *phosphite*, Na_2HPO_3 .

If the gas is bubbled through water, each bubble takes fire as it reaches the air, forming a vortex ring of white smoke (*phosphoric oxide*, P_4O_{10}).

Pure phosphine, though it readily burns, is not spontaneously inflammable; the impure gas made in the way just described is ignited by the spontaneous combustion of traces of the vapour of the liquid hydride, P_2H_4 . If alcoholic potash is substituted for aqueous alkali, the liquid hydride is not formed and the phosphine does not then take fire on reaching the air.

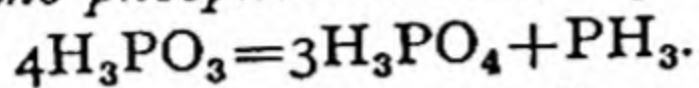
Other methods of obtaining phosphine are:

- (i) By the action of water on *calcium phosphide*, Ca_3P_2 :



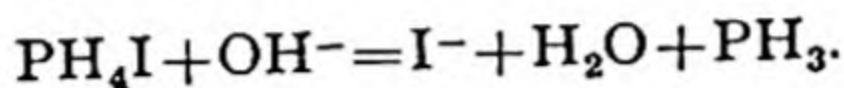
(Impure and spontaneously inflammable.)

- (ii) By heating *ortho-phosphorous acid*, H_3PO_3 :



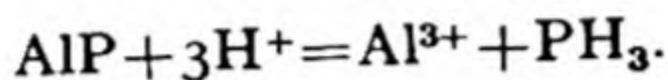
(Fairly pure; not spontaneously inflammable.)

- (iii) By warming *phosphonium iodide*, PH_4I , with dilute caustic alkali:



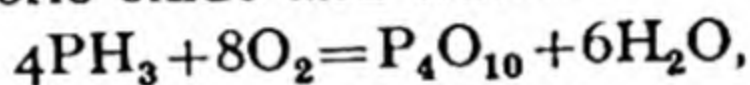
(Pure.)

- (iv) By the action of dilute sulphuric acid on *aluminium phosphide*, AlP :

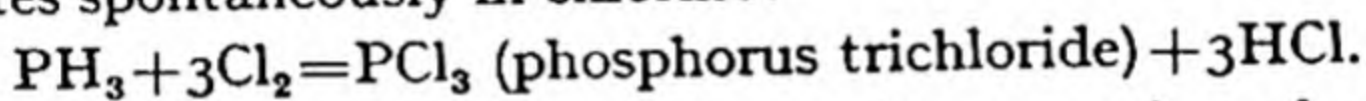


(Pure.)

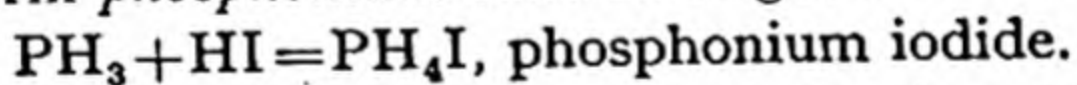
Phosphine is a colourless, poisonous gas, with an unpleasant smell which has been likened to that of garlic.* It burns readily in air, forming phosphoric oxide and water:



and ignites spontaneously in chlorine:



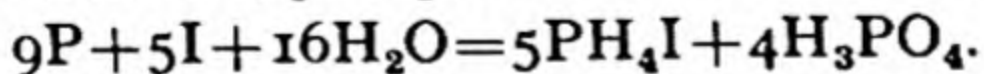
It is sparingly soluble in water (5 c.c. in 100 c.c.), and neutral to litmus; it will, however, combine directly with gaseous halogen hydrides to form *phosphonium salts* analogous to ammonium salts:



When passed into solutions of metallic salts, phosphine often gives precipitates of the metal or the metallic phosphide or both.

On sparking, phosphine is decomposed into its elements, 2 volumes of the gas giving 3 volumes of hydrogen. The vapour density is 17, hence the molecular weight is 34 and the formula PH_3 .

Phosphonium iodide, PH_4I , is a lustrous white crystalline solid best made by adding iodine to a solution of yellow phosphorus in carbon disulphide, distilling off the solvent in a current of carbon dioxide, and adding the calculated amount of water to the residue. On warming the mixture, phosphonium iodide sublimes:

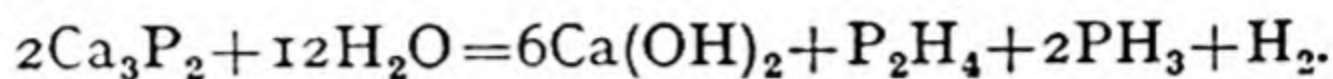


Phosphonium iodide dissociates on heating, or dissolving in water:



* A base libel on a plant recommended by the Father of Chemistry, HERMES, to ODYSSEUS, as an antidote to the poisons of CIRCE.

Diphosphorus tetrahydride, liquid phosphorus hydride, P_2H_4 , is a colourless, spontaneously inflammable liquid obtained, with phosphine and hydrogen, by the action of water on commercial calcium phosphide:

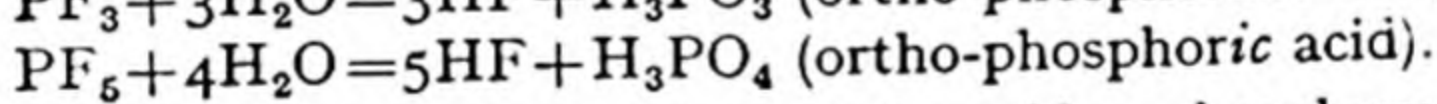
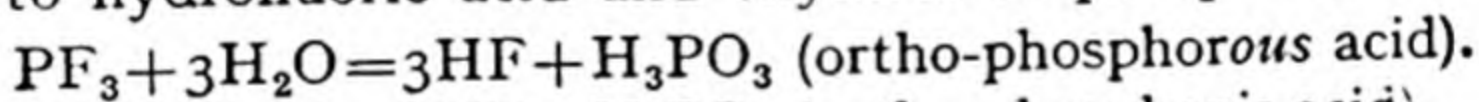


On passing the mixture of products through a U-tube surrounded by a freezing-mixture, the liquid hydride (B.P. 58°) collects. In formula it resembles hydrazine, N_2H_4 , from which, however, it differs in its readier inflammability and its completely non-basic character.

Phosphorus halides. Phosphorus forms two series of compounds with the halogens; in one series it is *tervalent* and in the other series *quinquevalent*. The following halides (among others) are known:

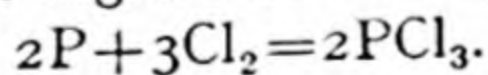
Phosphorus	Fluorides	Chlorides	Bromides	Iodide
Tervalent Quinquevalent	PF_3 , gas PF_5 , gas	PCl_3 , liquid PCl_5 , solid	PBr_3 , liquid PBr_5 , solid	PI_3 , solid

Phosphorus fluorides. Both phosphorus trifluoride and phosphorus pentafluoride are colourless, fuming gases, hydrolysed by water to hydrofluoric acid and oxyacids of phosphorus:

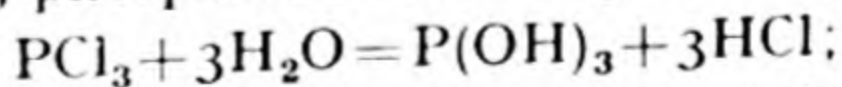


Unlike the pentachloride and pentabromide, phosphorus pentafluoride does not dissociate when heated.

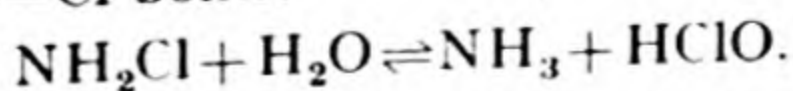
Phosphorus trichloride, PCl_3 , is a colourless, fuming liquid (B.P. 76° , M.P. -112°) prepared by passing a current of dry chlorine over phosphorus (either allotrope) and collecting the product in a cooled distilling-flask the side neck of which is fitted with a calcium chloride tube, to prevent ingress of atmospheric moisture:



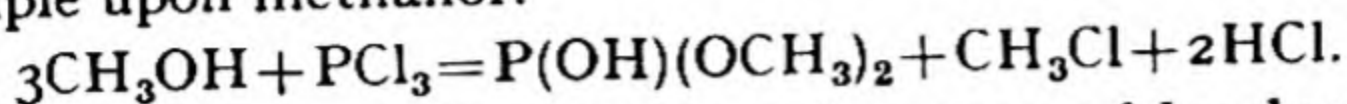
Phosphorus trichloride is very vigorously hydrolysed by water; on mixing it with ice, phosphorous acid is produced:



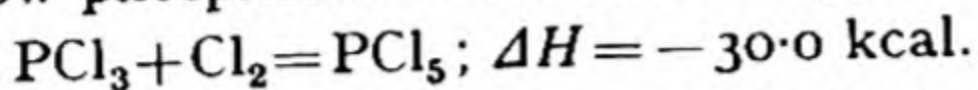
but if the temperature is uncontrolled much of the phosphorous acid is disproportionated to phosphoric acid and phosphine (p. 465, ii). The hydrolysis of the P—Cl bond to P—OH and HCl is contrasted with that of the N—Cl bond:



Upon alcohols the action of phosphorus trichloride is not simple; for example upon methanol:

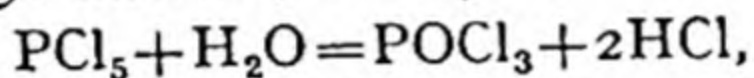


Phosphorus pentachloride, PCl_5 , can be prepared by dropping the trichloride into a vessel through which a slow current of chlorine is passed; or by bubbling chlorine through the trichloride or a solution of yellow phosphorus in carbon disulphide:

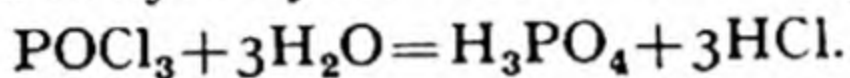


It is a pale yellow solid which sublimes at 100° – 160° , but can be melted under pressure at 148° . The vapour shows the greenish colour of chlorine, owing to dissociation, and since the dissociation is endothermic (see equation above) it is favoured by rise of temperature, becoming complete at about 300° .

Phosphorus pentachloride fumes in moist air, and reacts violently with water. The first stage in the hydrolysis is *phosphorus oxychloride* or *phosphoryl chloride*, POCl_3 :

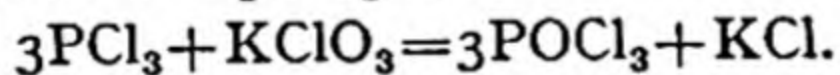


but this oily liquid is hydrolysed further to *orthophosphoric acid*:



Phosphorus pentachloride was formerly much used to replace the hydroxyl group with chlorine in organic compounds (e.g. in the preparation of acyl chlorides), but its action, like that of the trichloride (see above), is in many cases not confined to that simple replacement. It has long been superseded for that purpose by thionyl chloride, SOCl_2 (p. 522), which combines the merits of cheapness, greater regularity of action, and the convenience of a gaseous product (sulphur dioxide).

Phosphoryl chloride, POCl_3 , is prepared by the action of potassium chlorate upon well-cooled phosphorus trichloride:



It boils at 108° , and with water yields orthophosphoric and hydrochloric acids.

Phosphorus tribromide, PBr_3 , is a colourless, fuming liquid, B.P. 172° .

Phosphorus pentabromide, PBr_5 , is a yellow crystalline solid which dissociates on heating.

Phosphorus iodides, e.g. PI_3 and P_2I_4 , are used as sources of hydrogen iodide, which they yield on hydrolysis; and as iodinating agents, e.g. in the preparation of alkyl iodides.

Phosphorous oxide, P_4O_6 , is obtained by burning phosphorus in a regulated, insufficient supply of air. A suitable apparatus is shown diagrammatically in Fig. 88. A slow current of air is drawn

through the apparatus, and the phosphorus is ignited by gently warming it. A mixture of phosphorous oxide, phosphoric oxide, and phosphorus vapour passes into the condenser, which is maintained at about 50° ; here the last two condense and are withheld by the plug of glass wool, while the phosphorous oxide vapour travels on to the U-tube, in which it condenses to a white solid. When sufficient has collected, it is melted and

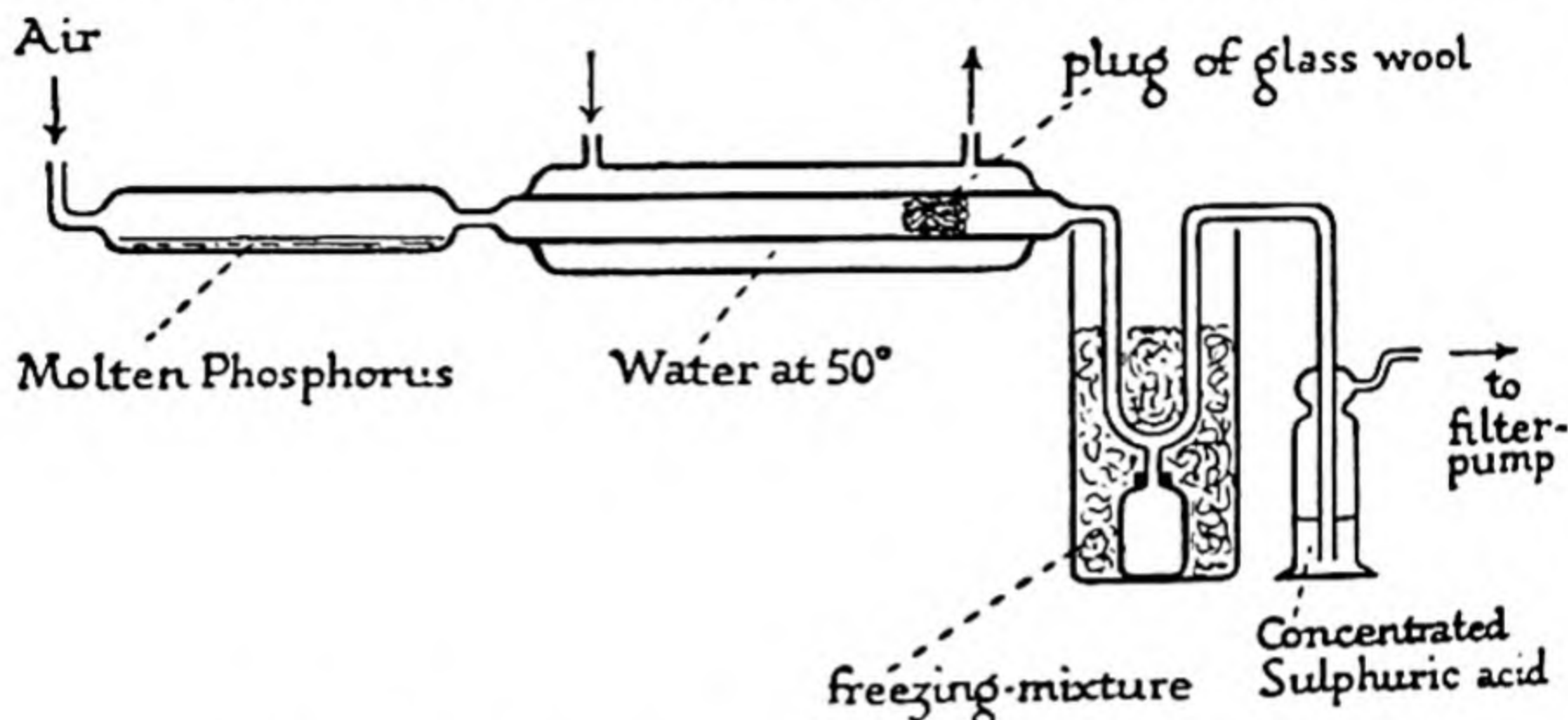
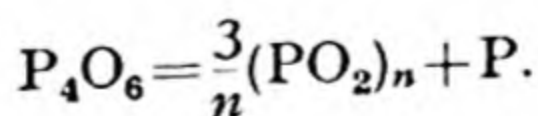


FIG. 88. PREPARATION OF PHOSPHOROUS OXIDE

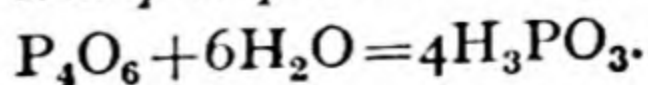
allowed to run down into the bottle. It may be purified by distillation in an inert atmosphere, or by recrystallization from carbon disulphide.

Phosphorous oxide is a colourless, waxy, crystalline solid (M.P. 24° , B.P. 173°). Like many other phosphorus compounds, it has an unpleasant smell and is very poisonous. The vapour density and X-ray examination of the solid show a molecular formula P_4O_6 in both states. The molecule is a tetrahedral 'cage' with phosphorus at the four apices, as in elementary phosphorus (p. 121), and oxygen just outside the mid points of the six edges.

On exposure to air it oxidizes rapidly, taking fire when heated slightly above its melting-point. The product is chiefly phosphoric oxide, P_4O_{10} , but usually contains some of another oxide $(PO_2)_n$ as well. The polymeric dioxide is also formed, together with red phosphorus, when phosphorous oxide is strongly heated in the absence of air:

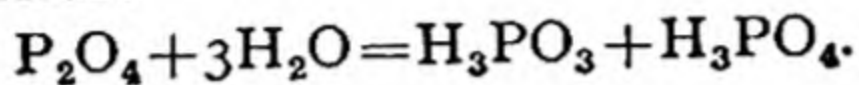


When added to cold water phosphorous oxide slowly dissolves, forming a solution of *orthophosphorous acid*, H_3PO_3 :



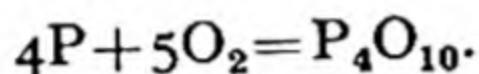
With hot water it reacts energetically, to give a variety of products, including *orthophosphoric acid*, H_3PO_4 , phosphine, and red phosphorus.

The polymeric dioxide, $(\text{PO}_2)_n$, obtained as described above, can be sublimed away from the red phosphorus formed at the same time. It is a colourless crystalline solid which sublimes at 180° . On solution in water it yields a mixture of orthophosphorous and orthophosphoric acids:



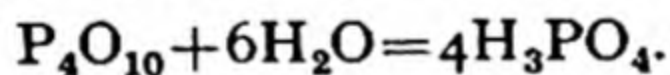
Its vapour density indicates a molecule P_4O_8 , but the solid has not been investigated.

Phosphoric oxide, P_4O_{10} , is formed when phosphorus is burned in a free supply of air or oxygen:

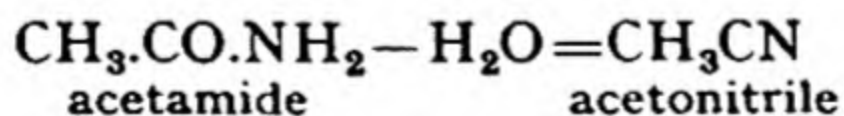
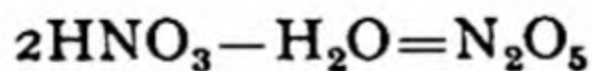


The crude oxide so prepared contains phosphorous oxide and red phosphorus; it may be purified by oxidizing the impurities to P_4O_{10} , e.g. by subliming it in a current of dry oxygen over a platinum catalyst.

Phosphoric oxide is a white, silky, crystalline powder. It sublimes at about 250° – 300° , giving a vapour the density of which shows it to consist of P_4O_{10} molecules, and X-ray examination of the solid indicates a 'cage' molecule like P_4O_6 with an extra atom of oxygen linked to each phosphorus atom and projecting outwards from the centre of the tetrahedron. Its principal property is its extreme affinity for water. If left exposed to the air, it rapidly deliquesces to a sticky mass of phosphoric acids. On boiling the solution, and more slowly on allowing it merely to stand, these acids are finally converted into orthophosphoric acid, H_3PO_4 :



Phosphoric oxide is widely used as a drying agent for removing the last traces of water from gases and liquids, and as a dehydrating agent for withdrawing the elements of water from various compounds, e.g.:

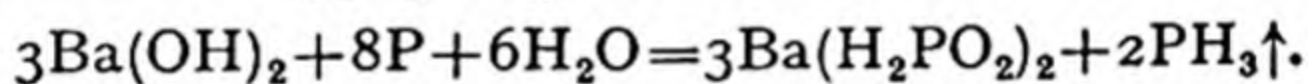


Its efficacy as a drying agent depends partly on the fact that the phosphoric acids formed when it combines with water are very stable compounds and show no tendency to dissociate into phosphoric oxide and water.

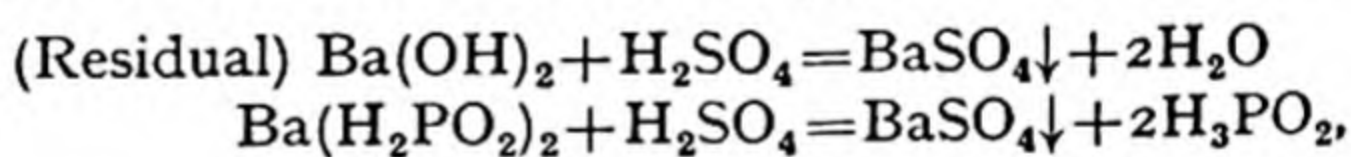
Oxyacids of Phosphorus. Phosphorus forms numerous oxyacids, the chief of which, together with the corresponding oxides or anhydrides, are shown in the following table:

Oxide	Acid
—	H_3PO_2 , hypophosphorous acid
Phosphorous	$\left. \begin{array}{l} \text{H}_3\text{PO}_3 \text{ ortho-} \\ \text{H}_4\text{P}_2\text{O}_5 \text{ pyro-} \\ \text{HPO}_2 \text{ meta-} \end{array} \right\}$ phosphorous acid
Phosphoric	$\left. \begin{array}{l} \text{H}_3\text{PO}_4 \text{ ortho-} \\ \text{H}_4\text{P}_2\text{O}_7 \text{ pyro-} \\ (\text{HPO}_3)_n \text{ meta-} \end{array} \right\}$ phosphoric acid

Hypophosphorous acid, H_3PO_2 . *Hypophosphites*, salts of hypophosphorous acid, are formed when yellow phosphorus is heated with a solution of an alkali. If barium hydroxide is selected as the alkali, barium hypophosphite is formed:



The exact quantity of sulphuric acid required to convert all the barium in the solution into barium sulphate is now added:



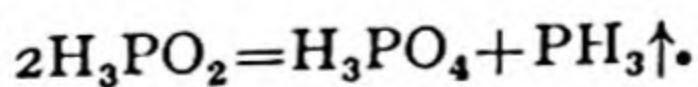
and after filtration from the precipitated barium sulphate, the solution of hypophosphorous acid is evaporated, preferably under reduced pressure.

Hypophosphorous acid is a colourless crystalline solid which melts at $18^\circ\text{--}20^\circ$, i.e. at about room temperature. It is a moderately strong

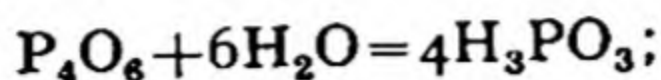
monobasic acid, of which the anion has the structure $\text{O}=\text{P}^{\vee}\begin{array}{l} \diagup \text{H} \\ \text{---} \text{H} \\ \diagdown \text{O}^- \end{array}$. Both

the acid and its salts are powerful reducing agents, since they are easily oxidized to phosphorous acid (or phosphites) and still further to phosphoric acid (or phosphates). Thus they reduce mercuric chloride to mercurous chloride and mercury, and copper sulphate to copper and *cuprous hydride*, CuH .

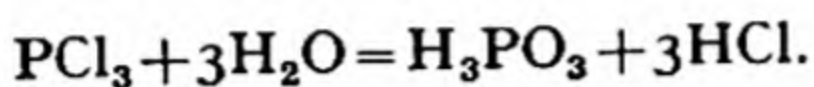
On heating, hypophosphorous acid decomposes into phosphoric acid and phosphine:



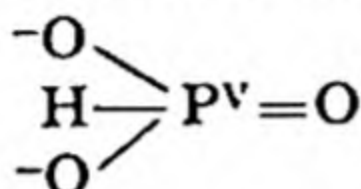
Phosphorous acids. Phosphorous oxide slowly reacts with cold water to form *orthophosphorous acid*, H_3PO_3 :



but this substance is more readily obtained by the hydrolysis of phosphorus trichloride (p. 466):

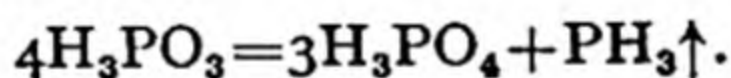


It is a white crystalline solid (M.P. 70°), and is very soluble in water. Towards alkalis it behaves as a dibasic acid, and its anion has the structure



It is noteworthy that two isomeric esters of this acid have been obtained: the one (B.P. 156°) undoubtedly has the constitution $\text{P}(\text{OC}_2\text{H}_5)_3$, while the other (B.P. 198°) is presumably $\text{C}_2\text{H}_5\text{PO}(\text{OC}_2\text{H}_5)_2$, a derivative of the structural form shown above. In titrating a solution of orthophosphorous acid with sodium hydroxide solution, methyl orange changes colour at a point corresponding to the formation of the *monosodium* salt, NaH_2PO_3 , and phenolphthalein changes colour when the *disodium* salt, Na_2HPO_3 , is formed.

When orthophosphorous acid is heated it decomposes into orthophosphoric acid and phosphine:



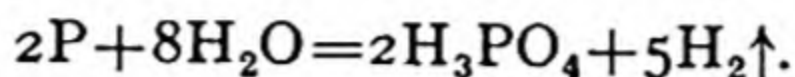
Both the acid and its salts are energetic reducing agents, since they readily combine with oxygen to form phosphoric acid or phosphates. They will, for example, precipitate gold, silver, and copper from solutions of the metallic salts, and will reduce mercuric chloride to mercurous chloride.

Pyrophosphorous acid, $\text{H}_4\text{P}_2\text{O}_5$, is a colourless crystalline solid made by the action of phosphorus trichloride on orthophosphorous acid. *Metaphosphorous acid* is a similar solid obtained by the action of oxygen on phosphine at low pressure. Both the pyro- and the meta-acids readily combine with water to yield orthophosphorous acid.

Phosphoric acids. *Orthophosphoric acid*, H_3PO_4 , is prepared in the laboratory, and also industrially, by dissolving phosphoric oxide in water and boiling the solution:

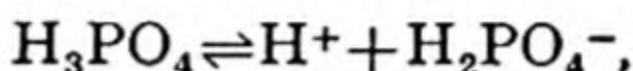


It is also manufactured by heating phosphorus with steam under pressure, in the presence of nickel as a catalyst:

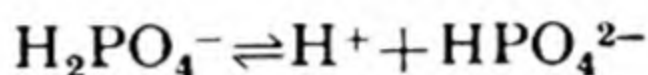


In the laboratory it is usually prepared by heating red phosphorus with fairly concentrated nitric acid (specific gravity 1.2) and evaporating the solution in a platinum basin. The concentrated acid attacks porcelain.

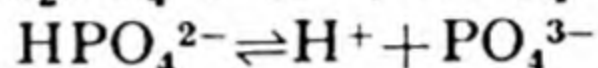
Orthophosphoric acid is a white, crystalline, deliquescent solid (M.P. 42°), readily soluble in water. It behaves as a tribasic acid, though only the first dissociation:



takes place to any great extent. The second and third dissociations:



and

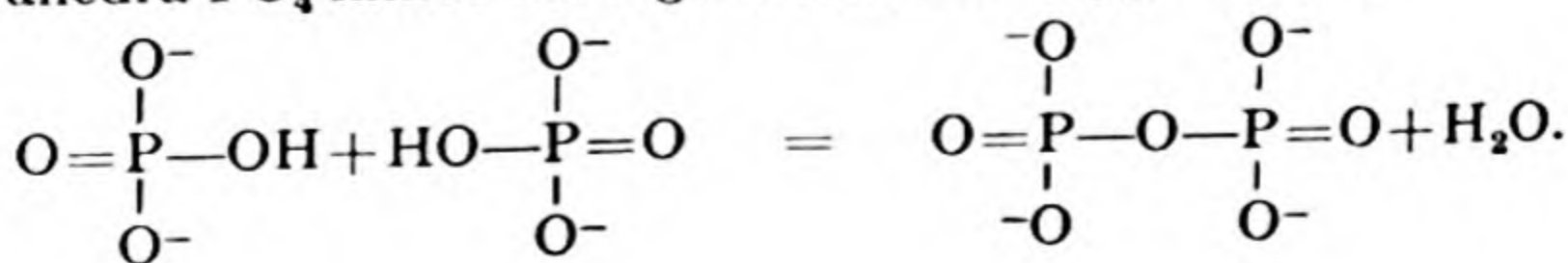


occur much less readily. Of the three sodium salts, NaH_2PO_4 is neutral to methyl orange (i.e. the pH of its solution is about 4–5), Na_2HPO_4 is alkaline to methyl orange but neutral to phenolphthalein (pH 9–10), and Na_3PO_4 is strongly alkaline (pH about 12).

The disodium phosphate, which crystallizes as its *dodecahydrate*, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, is the common 'sodium phosphate' of the laboratory. The trisodium salt—also a dodecahydrate, $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ —is an excellent and widely used detergent (e.g. in soap powders), and is also employed as a water-softener. *Calcium hydrogen phosphate*, CaHPO_4 , is used as a flour preservative. For *calcium 'superphosphate'*, $\text{Ca}(\text{H}_2\text{PO}_4)_2$, see p. 345. *Ammonium dihydrogen orthophosphate*, $\text{NH}_4\text{H}_2\text{PO}_4$, is used to render wood fireproof. *Microcosmic salt*, or *sodium ammonium hydrogen orthophosphate tetrahydrate*, $\text{NaNH}_4\text{HPO}_4 \cdot 4\text{H}_2\text{O}$, is occasionally substituted for borax in the 'bead' test in qualitative analysis. On heating, it loses water and ammonia, and yields a glassy bead of sodium polymetaphosphate (see below).

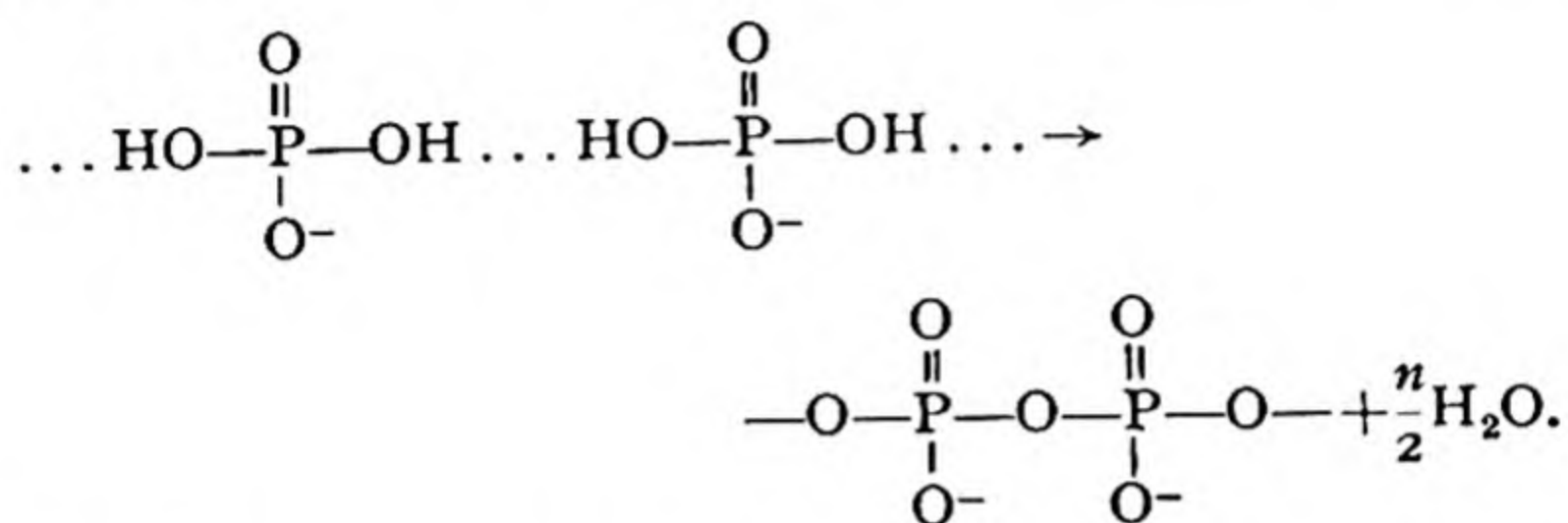
Condensed Phosphates.

Pyrophosphates. When disodium hydrogen phosphate, Na_2HPO_4 , is heated above 300° water is lost and *sodium pyrophosphate*, $\text{Na}_4\text{P}_2\text{O}_7$, remains, in which the anion consists of two orthophosphate tetrahedra PO_4 linked through a common oxygen atom:

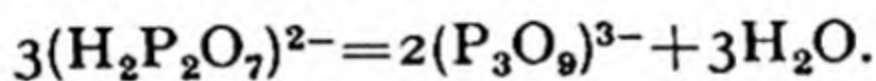


Sodium pyrophosphate crystallizes from water as $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$. From a solution in acetic acid the dihydrogen salt, $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7 \cdot 6\text{H}_2\text{O}$, separates. Baking-powder is a mixture of the latter salt with sodium bicarbonate; the two salts do not interact in the cold, but carbon dioxide is liberated on heating.

Metaphosphates. On thermal dehydration of a salt, such as NaH_2PO_4 , in which the anion contains *two* hydroxyl groups, condensation of PO_4 tetrahedra can proceed further, since now each original tetrahedron can become bound by common oxygen atoms to *two* others:



The extent of condensation is determined mainly by the temperature at which dehydration is effected, but also by the salt type: sodium dihydrogen pyrophosphate, $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$, heated at 300° yields *sodium trimetaphosphate*, $\text{Na}_3\text{P}_3\text{O}_9$, in which the anion consists of three tetrahedra linked in a closed ring:

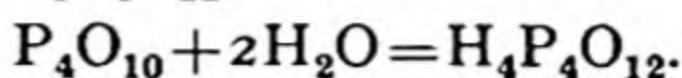


Fusion above 600° of any of the salts— NaH_2PO_4 , $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$, or *microcosmic salt*, $\text{NaNH}_4\text{HPO}_4$ (which gives NaH_2PO_4 by loss of ammonia)—yields on cooling *sodium polymetaphosphate*, or 'metaphosphate glass' (erroneously termed 'hexametaphosphate'). In this substance the anion is macromolecular and co-extensive with the crystal: every PO_4 tetrahedron having become linked to two others to give an indefinitely large anion, of composition expressible as $(\text{PO}_3)_n^{n-}$.

In spite of the size of its anion, sodium polymetaphosphate is very soluble in water, and the solution is invaluable for dissolving calcium carbonate and sulphate deposited as 'boiler-scale' in water-heating equipment. The polymetaphosphate is also marketed as a most efficient water softener: its great merit is that no insoluble matter is produced by its softening action. There is little doubt that these beneficial effects are due to the power of the large polymetaphosphate anion to enmesh calcium ions within its structure.

When the solution formed by adding phosphoric oxide gradually

to ice-cold water is neutralized with sodium hydroxide, *sodium tetrametaphosphate*, $\text{Na}_4\text{P}_4\text{O}_{12}$, is obtained:



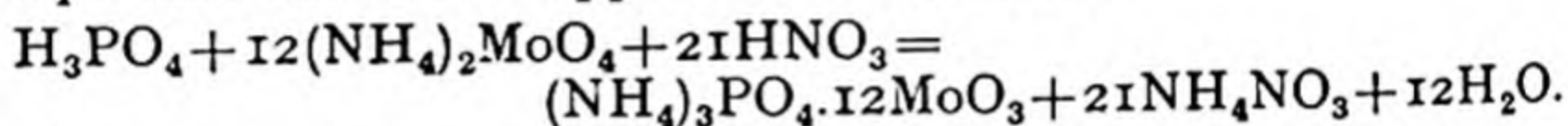
In the anion $(\text{P}_4\text{O}_{12})^{4-}$ four phosphate tetrahedra are linked in a closed ring.

In acid solution all condensed phosphates are hydrolysed, slowly at ordinary temperature and rapidly on boiling, to orthophosphate as the final product.

Tests for Phosphates.

The phosphates of the alkali metals (and ammonium) are soluble in water; most other phosphates are insoluble in water but soluble in dilute mineral acids.

1. Solutions of phosphates give a yellow precipitate on warming with an excess of *ammonium molybdate* solution and nitric acid. The composition of the precipitate, *ammonium phosphomolybdate*, varies somewhat with the conditions, but the following equation shows the approximate reaction:

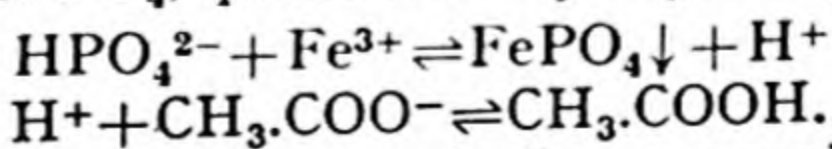


Arsenates give a similar precipitate of ammonium arsenomolybdate, but much more slowly and only on boiling.

2. Addition of *silver nitrate* to a neutral solution of an *orthophosphate* causes the precipitation of *silver orthophosphate*, Ag_3PO_4 . This is a yellow substance, readily soluble in ammonia solution and in dilute nitric acid.

Pyro- and *meta-*phosphates give *white* precipitates with silver nitrate; but an acidified solution of a polymetaphosphate coagulates *egg-albumen*, while a similar solution of a pyrophosphate does not.

3. *Magnesia mixture* (i.e. a solution of magnesium chloride, ammonium chloride, and ammonia) gives with orthophosphates a white crystalline precipitate of hexahydrated *magnesium ammonium orthophosphate*, $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$. *Arsenates* give a similar precipitate of magnesium ammonium arsenate.
4. *Phosphate Separation*. If sodium phosphate solution is buffered (p. 227) with sodium acetate, ferric chloride will precipitate the PO_4 , quantitatively as *ferric phosphate*, FePO_4 :



If the solution is not buffered, the accumulation of hydrogen ions prevents complete precipitation of the FePO_4 .

This reaction is used for removing phosphates in qualitative analysis.

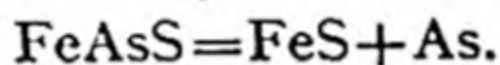
ARSENIC, As

Atomic number: 33. *Atomic weight:* 74.91. *Specific gravity:* 5.73.
Melting-point: 814° (under 36 atmospheres pressure).
Boiling-point: — (sublimes at 615°).

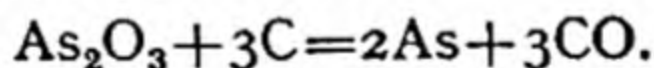
History. Yellow arsenic sulphide (As_2S_3) was employed as a pigment by the ancient Assyrians, whence its name *sandarach*, from *sindu arque*, 'yellow paint.' Both realgar (As_2S_2) and sandarach were employed by the Alexandrian and later alchemists, and the Arabs were able to extract the element arsenic from them. The resemblance between sandarach and stibnite (antimony sulphide, Sb_2S_3) was pointed out as early as the thirteenth century. The metallic character of arsenic was established by HENCKEL (1725), BRANDT (1733), and MONNET (1774).

Occurrence. Many sulphide ores (e.g. iron pyrites, copper pyrites) contain appreciable quantities of arsenical compounds, but the chief natural arsenic minerals are *realgar* (As_2S_2), *sandarach* or *orpiment* (As_2S_3), *mispickel* (FeAsS), and *cobaltite* (CoAsS). The last two are sulpharsenides. Arsenic also occurs as the free element, in small quantity, and traces of arsenic compounds are very widely diffused in nature.

Extraction. Arsenic is usually obtained by heating mispickel:



The arsenic sublimes and is collected in sheet-iron conical condensers. It may also be obtained by roasting the sulphide ores, to convert them into arsenious oxide, As_2O_3 , and then reducing the oxide by heating it with charcoal:



Properties. Arsenic exists in three allotropic forms:

α -arsenic, or *yellow arsenic*, is made by the very rapid cooling of arsenic vapour mixed with some inert gas such as carbon dioxide. It is a translucent, yellow, crystalline solid, readily soluble in carbon disulphide. In the air it oxidizes spontaneously, glowing in the dark and emitting a garlic-like smell. At ordinary temperatures it is metastable, and rapidly passes into the ordinary form, *γ -arsenic*, or *grey arsenic*. From the elevation of the boiling-point of its solutions in carbon disulphide, it may be shown to have the formula As_4 . Specific gravity = 2.1.

β -arsenic, or *black arsenic*, is formed, together with *γ -arsenic*, when arsenic vapour is slowly cooled, and when *α -arsenic* is allowed to stand. It gradually passes into the *γ* form, especially on warming. Specific gravity = 4.6.

γ-arsenic, grey arsenic, or metallic arsenic, is the ordinary form of the element. It is somewhat metallic in appearance, and is a fairly good conductor of electricity, but is brittle. Specific gravity = 5.73.

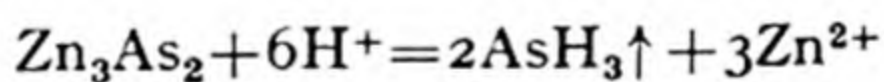
When heated, arsenic sublimes, giving a yellow vapour the density of which corresponds to As_4 molecules up to about 800° . Above this temperature dissociation occurs into As_2 molecules. The molecule As_4 is tetrahedral, like that of yellow phosphorus (p. 121).

If heated in the air or in oxygen, arsenic burns, forming arsenious oxide, As_2O_3 (properly As_4O_6 ; see below). It also combines readily with the halogens and with sulphur. Since its electrode potential (p. 242) is +0.3, it falls below hydrogen in the electrochemical series and therefore will not dissolve in dilute non-oxidizing acids. It is, however, converted by hot concentrated sulphuric acid into arsenious oxide, and by hot concentrated nitric acid into arsenic acid, H_3AsO_4 .

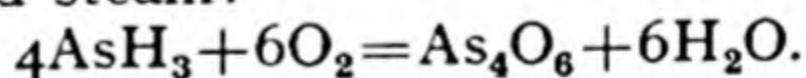
All arsenic compounds (like the element itself) are intensely poisonous; hence great care should be taken in working with them—particularly if they are gaseous.

COMPOUNDS OF ARSENIC

Arsenic hydride, hydrogen arsenide, arsine, AsH_3 . Arsenic hydride may be obtained by the action of nascent hydrogen upon arsenic itself, or upon a solution of an arsenic compound. To prepare a pure specimen, it is best to act upon an arsenide (e.g. zinc arsenide or calcium arsenide) with dilute hydrochloric or sulphuric acid:



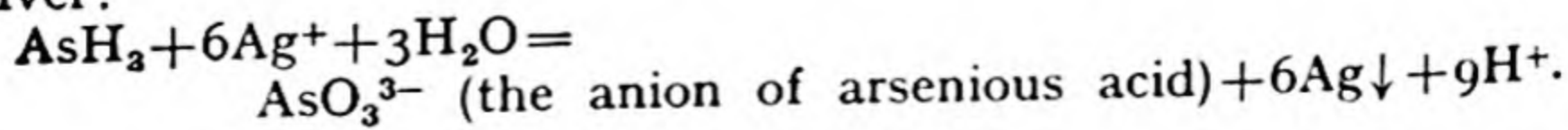
It is a colourless, *very dangerously* poisonous, evil-smelling gas, which can be condensed to a colourless liquid boiling at -55° . In a plentiful supply of air it burns with a pale violet flame, forming arsenious oxide and steam:



On heating or sparking it decomposes into arsenic and hydrogen. It is found that 2 volumes of arsenic hydride yield 3 volumes of hydrogen, hence by Avogadro's principle the formula of the gas must be As_nH_3 . The V.D. is 78, and since the A.W. of arsenic is 75, n must equal 1.

The decomposition of arsenic hydride by heat is the basis of Marsh's test for detecting the element (p. 479).

Arsenic hydride reacts with silver nitrate solution, yielding first a yellow compound, $\text{Ag}_3\text{As} \cdot 3\text{AgNO}_3$, and finally depositing metallic silver:

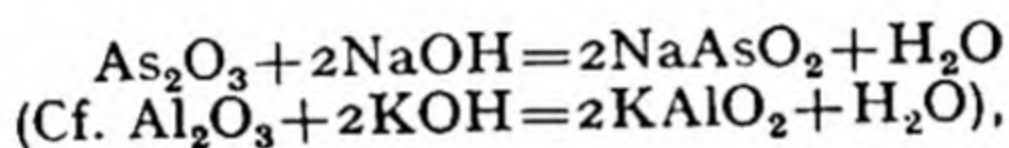


Hydrogen contaminated with the gas (as, for instance, it may be when prepared from commercial zinc and sulphuric acid) may thus be purified by bubbling through silver nitrate solution.

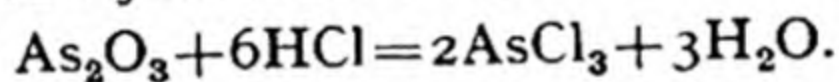
Arsenious oxide, otherwise known as arsenic trioxide or white arsenic, is formed when arsenic, or either of the sulphides of arsenic, is burned in air or oxygen. Commercially it is obtained as a by-product in the extraction of metals from their arseniferous ores.

It exists in two different crystalline modifications (*rhombic* and *octahedral*, the latter being the stable form), and an amorphous, glassy form which is probably macromolecular. It dissolves slightly in water (about 18 gm.-litre at room temperature) to give a feebly acid solution supposed to contain arsenious acid, H_3AsO_3 . Vapour-density determinations show that the vapour of arsenious oxide consists of As_4O_6 molecules; investigation by X-ray diffraction has shown that solid arsenious oxide also consists of these molecules, so to write its formula as As_2O_3 is justifiable only on the ground of convenience.

Chemically arsenious oxide behaves as an *amphoteric* oxide. Thus it dissolves in sodium hydroxide solution to form sodium meta-arsenite:



and in concentrated hydrochloric acid to form arsenic trichloride:

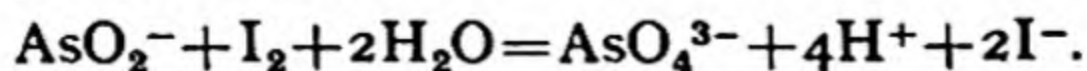


When dry crystals of arsenious oxide are shaken together, they emit light (*triboluminescence*).

Arsenic oxide is the name usually applied to the final product of the strong ignition of arsenic acid (p. 478), but for complete dehydration, temperatures are necessary at which the pentoxide begins to lose oxygen to give arsenious oxide: hence *pure* arsenic oxide has probably not been prepared.

Arsenious acids, H_3AsO_3 and HAsO_2 . Arsenious acids themselves have not been isolated, but arsenites are well known and important. Like the phosphites, they exist in *ortho* and *meta* forms, the *ortho*-arsenites being salts of the supposititious *ortho*-arsenious acid, H_3AsO_3 , while the *meta*-arsenites are salts of the equally elusive *meta*-arsenious acid, HAsO_2 .

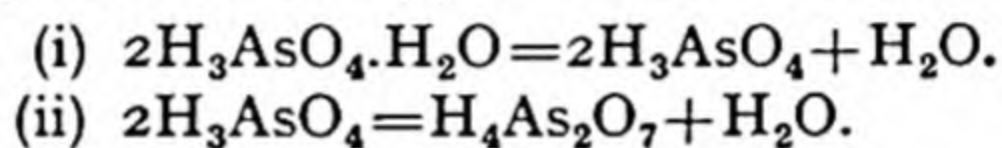
Sodium meta-arsenite, NaAsO_2 , is made by dissolving arsenious oxide in hot sodium hydroxide or sodium carbonate solution. It is used industrially as a weed-killer, and in the laboratory as a reducing agent in volumetric analysis, e.g. for the estimation of iodine, which oxidizes it to sodium arsenate:



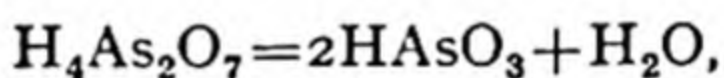
In this titration (which may also serve, conversely, for the estimation of sodium arsenite) the solution must be buffered by addition of sodium bicarbonate. In acid solution arsenates act as mild oxidizing agents, and can oxidize iodide ions, I^- , to free iodine. In this property arsenates differ notably from phosphates (see also p. 480, 5(a)).

Cupric hydrogen arsenite, $CuHAsO_3$, or SCHEEL'S Green, is obtained as a green precipitate when copper sulphate is added to a solution of sodium arsenite. It was formerly used as a pigment for wall-papers, a somewhat rash proceeding which brought profit to more than one undertaker. It still finds limited application as an insecticide.

Arsenic acids. When arsenious oxide is boiled with concentrated nitric acid, the solution on cooling deposits colourless crystals of *ortho*-arsenic acid hemihydrate, $2H_3AsO_4 \cdot H_2O$. On heating to 100° , this loses its water of hydration, while at 180° part of the water of composition is given off, and *pyro*-arsenic acid is obtained:

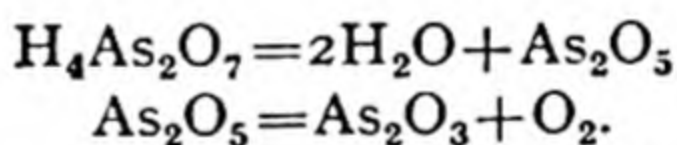


It is possible that, at a slightly higher temperature, *meta*-arsenic acid is produced:



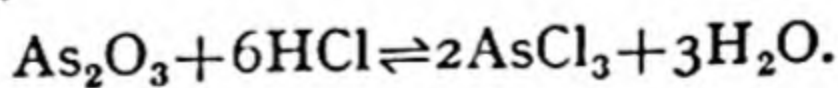
though the authorities are not agreed on this point.

Still further heating yields a mixture of arsenic and arsenious oxides (p. 477):

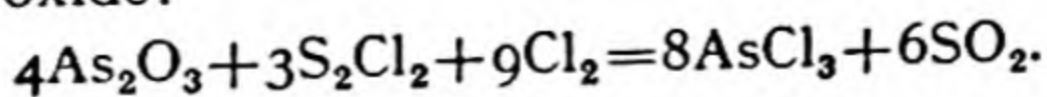


Pyro- and *meta*-arsenates are known only in the solid form. On solution in water they are immediately converted into *ortho*-arsenates. As mentioned above, arsenates are isomorphous with the corresponding phosphates, so that they presumably have similar constitutions.

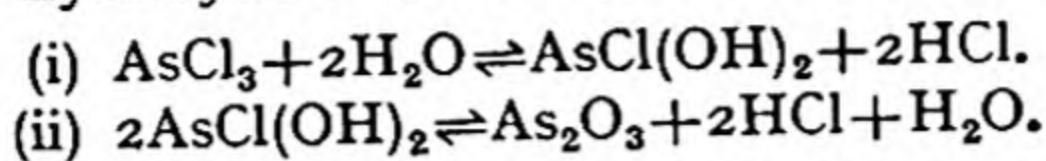
Arsenic trichloride, $AsCl_3$, is a colourless, oily, poisonous liquid boiling at 130° . It can be obtained by heating arsenic in chlorine, by distilling a mixture of sodium chloride, arsenious oxide, and concentrated sulphuric acid, or by the action of hydrogen chloride on arsenious oxide:



It is, however, best prepared by PARTINGTON'S method, which consists in passing chlorine into a mixture of disulphur dichloride and arsenious oxide:



Arsenic trichloride fumes in moist air and is hydrolysed by water; the degree of hydrolysis increases on dilution:



AsCl(OH)_2 is known as *arsenic hydroxychloride*.

Tests for Arsenic and its Compounds.

I. MARSH'S Test (1836). If arsenic or an arsenic compound is added to a solution in which hydrogen is being generated, arsenic hydride is evolved. This can be detected by passing

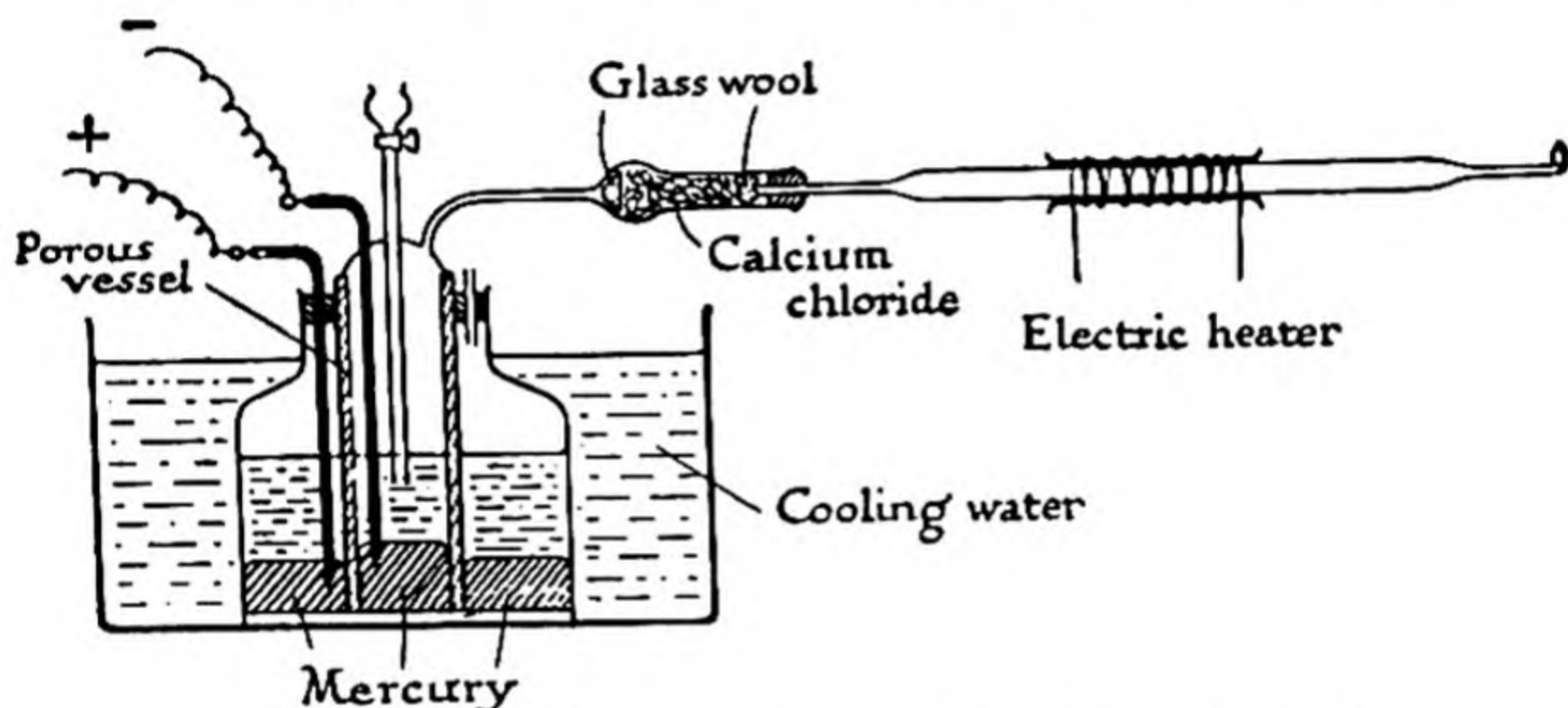


FIG. 89. MARSH'S TEST FOR ARSENIC (ELECTROLYTIC)

the issuing gas-mixture through a hot tube, when a black deposit of metallic arsenic is formed just beyond the heated portion. By comparing this deposit with similar deposits obtained under standard conditions, the weight of arsenic in the material under examination can be accurately estimated.

For qualitative purposes in the laboratory, the hydrogen is generated from zinc and dilute sulphuric acid in a Woulfe bottle or other convenient apparatus, and ignited at a jet. The flame is allowed to impinge on cold porcelain, where, if arsenic hydride is present in the gas, a black stain of arsenic is produced. Antimony forms a similar stain in the same circumstances, but the arsenic stain dissolves in bleaching-powder solution whereas the antimony stain does not.

For legal purposes, the hydrogen is generated electrolytically from arsenic-free dilute sulphuric acid in arsenic-free apparatus.

The substance to be tested is placed in a porous pot surrounding the cathode, and the whole apparatus is kept cool.

2. FLEITMANN'S Test, like Marsh's test, depends upon the formation of arsenic hydride in a solution generating hydrogen; but in this case the hydrogen is generated in *alkaline* solution. Under these conditions, antimony does *not* give antimony hydride.
3. REINSCH'S Test. Boil a strip of bright copper with the solution under test, acidified with concentrated hydrochloric acid. If arsenic is present, the copper becomes coated with a greyish film of copper arsenide. Dry, and heat in a test-tube: a white sublimate of As_2O_3 is formed.
4. ARSENITES give
 - (a) with hydrogen sulphide in acid solution: a yellow precipitate of arsenic trisulphide, As_2S_3 ;
 - (b) with silver nitrate in neutral solution: a yellow precipitate of silver arsenite (Ag_3AsO_3), soluble in dilute nitric acid and in ammonia solution;
 - (c) with copper sulphate: a precipitate of Scheele's Green.
 - (d) See test (b) for arsenates.
5. ARSENATES give
 - (a) with hydrogen sulphide in acid solution, slowly: a yellow precipitate of arsenic trisulphide and sulphur, the arsenate first being reduced to arsenite by the hydrogen sulphide; addition of a drop of aqueous potassium iodide greatly hastens the reduction, probably owing to the successive reactions:

$$\begin{aligned}\text{AsO}_4^{3-} + 2\text{I}^- + 2\text{H}^+ &= \text{AsO}_3^{3-} + \text{I}_2 \\ \text{I}_2 + \text{H}_2\text{S} &= 2\text{H}^+ + 2\text{I}^- + \text{S}\downarrow.\end{aligned}$$
 - (b) with ammonium molybdate and nitric acid: a yellow precipitate of ammonium arsenomolybdate, $(\text{NH}_4)_3\text{AsO}_4 \cdot 12\text{MoO}_3$, *on heating* (not in the cold—distinction from phosphates). Arsenites will also give this test, since the nitric acid oxidizes them to arsenates.

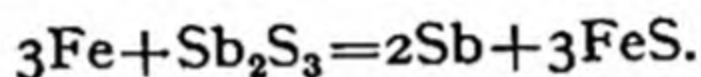
ANTIMONY, Sb

Atomic number: 51. Atomic weight: 121.76. Specific gravity: 6.6–6.7. Melting-point: 631°. Boiling-point, 1,380°.

History. Antimony occurs native, and is also easily extracted from its ore, so that it has been known from the beginnings of history. The name is probably derived from the Greek *anthemonion*, which was given to antimony sulphide (Sb_2S_3) on account of the appearance of the natural crystals, resembling the outspread petals of a flower (cf. *chrys-anthemum*, gold-flower). Under the name of *kohl*, or *ithmid*, antimony sulphide was—and is—used by Arab women as an eye-paint; and the symbol Sb is derived from the Latin modification of *ithmid*, viz. *stibium*.

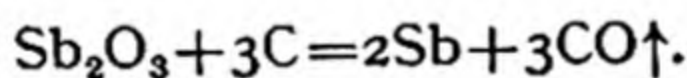
Occurrence. The sole important ore of antimony is the sulphide, Sb_2S_3 , which occurs naturally as *stibnite* in many parts of the world, but particularly in China, which produces about four-fifths of the total annual output.

Extraction. The crude ore is concentrated by liquation, i.e. by fusing the stibnite and running it off from the infusible earthy matter. The concentrated ore is then heated with iron:



The molten mass consists of two immiscible layers, the upper one being ferrous sulphide and the lower one antimony; the latter is tapped off and the metal purified by fusion with a little potassium nitrate and sodium carbonate.

In modern practice the stibnite is more frequently roasted in a current of air, and the resulting antimony oxide reduced by heating with charcoal:

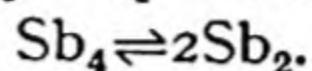


Properties. Antimony exists in two definite allotropic forms, viz. *grey*, or *metallic*, antimony, and *yellow* antimony. Two other so-called allotropes are probably either finely divided grey antimony ('black' antimony) or a mixture of antimony with antimony trichloride ('explosive' antimony).

Yellow antimony resembles the corresponding allotropes of phosphorus and arsenic, not merely in appearance, and in possessing greater reactivity than the more stable form, but in being soluble in carbon disulphide. It can be prepared by oxidizing liquid antimony hydride with chlorine or ozonized oxygen at -100° , and rapidly changes to grey antimony.

Grey, or *metallic*, antimony, is a soft, bluish-grey, distinctly crystalline metal, which melts at 631° , boils at $1,380^\circ$, and has a

specific gravity of 6.6–6.7. The vapour density at temperatures just above the boiling-point is slightly greater than 121.76, indicating that the molecules are partly Sb_4 but mainly Sb_2 :



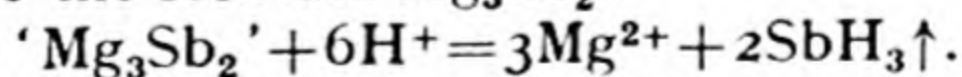
Antimony is unattacked by air at ordinary temperatures, and since it also expands slightly on solidification it is used for the manufacture of such cheap trinkets as can be cast in moulds. When strongly heated in air or oxygen, antimony takes fire and burns to the *trioxide*, Sb_2O_3 , with a little of the *tetroxide*, Sb_2O_4 . It combines energetically with the halogens (in the form of powder it ignites spontaneously in chlorine), and less energetically with sulphur and phosphorus.

Dilute acids are practically without action upon it, but hot concentrated sulphuric acid converts it into the *sulphate*, $\text{Sb}_2(\text{SO}_4)_3$, with evolution of sulphur dioxide, and concentrated nitric acid oxidizes it to hydrated *antimonic oxide*, Sb_2O_5 . In the presence of air and, more rapidly, in the presence of oxidizing agents such as potassium chlorate, it dissolves in hot concentrated hydrochloric acid, forming *chloroantimonic acid*, HSbCl_6 .

Uses. The principal use of antimony is in the manufacture of alloys, which, like the metal itself, expand on solidification and are therefore especially suitable for making printer's type from moulds. *Type metal* is of various kinds, commonly Pb, 82; Sb, 15; Sn, 3 per cent, or Pb, 70; Sb, 18; Sn, 10; Cu, 2 per cent. *Babbitt metal*, used for bearings, is Sn, 90; Sb, 7; Cu, 3 per cent. An *antifriction alloy* in general use is Sn, 75; Sb, 12.5; Cu, 12.5 per cent. Antimony is also an ingredient of rifle-bullet alloy and shrapnel alloy (p. 420), and of the alloy used for making accumulator plates (Pb, 94; Sb, 6 per cent). For *pewter*, see p. 420.

COMPOUNDS OF ANTIMONY

Antimony hydride or **stibine**, SbH_3 , is formed, like arsenic hydride, when the metal and its compounds are introduced into an *acid* mixture generating hydrogen; unlike arsenic hydride, however, it is *not* formed if the hydrogen-generating mixture is *alkaline* (cf. FLEITMANN'S test for arsenic, p. 480). It is best prepared by the action of dilute hydrochloric acid upon an alloy of magnesium and antimony in which the elements are present in a ratio roughly corresponding to the formula Mg_3Sb_2 :



It is a colourless, poisonous gas with a repulsive smell. On heating, and sometimes merely on standing, it explodes. It burns with a greyish flame, which will deposit a stain of metallic antimony on cold porcelain. This stain is unaffected by bleaching-powder solution (distinction from arsenic, p. 479).

Antimony hydride is not basic and will not dissolve in water. With silver nitrate solution it gives a black unstable precipitate said to be *silver antimonide*, Ag_3Sb .

Antimonious oxide, Sb_2O_3 , perhaps more generally known as *antimony trioxide*, may be obtained as a white crystalline solid by burning the metal or its sulphide in air or oxygen. If the temperature is sufficiently high, none of the tetroxide (q.v.) will be left in the product.

On heating, antimonious oxide melts at 656° and boils at $1,550^\circ$; the vapour density corresponds to that of a compound of formula Sb_4O_6 .

Antimonious oxide is very sparingly soluble in water, but is amphoteric and will dissolve in either acids or alkalis. Thus it dissolves in dilute hydrochloric acid to form the *trichloride*, SbCl_3 , and reacts with concentrated nitric and sulphuric acids to give a *basic nitrate* and the *normal sulphate* respectively. Potassium hydrogen tartrate solution dissolves it readily, forming *potassium antimonyl tartrate*, $2\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$, a very toxic salt used in medicine under the name of 'tartar emetic.' At the present day this substance is scarcely ever used as an emetic, but is injected into the blood to kill the protozoa which cause kala-azar and sleeping-sickness (trypanosomiasis).

In solutions of caustic alkalis, antimonious oxide dissolves to form salts of a very weak acid, probably of the composition HSbO_2 .

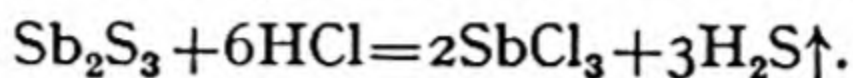
Antimony tetroxide, Sb_2O_4 , is formed when either the trioxide or the hydrated pentoxide is heated in the air to about 450° – 650° ; above this temperature it begins to decompose into the trioxide and oxygen. It is a white solid, very slightly soluble in water, to which it gives a weakly acid reaction.

Antimonates. On dehydrating the product of the oxidation of antimony with nitric acid, the oxide Sb_2O_5 is *not* obtained, since at the temperature necessary for complete dehydration, oxygen is also lost, and a mixture of tetroxide and trioxide results. The so-called 'pyro-antimonates' of sodium and potassium have been proved by X-ray analysis to have the constitution $\text{M}'\cdot\text{Sb}(\text{OH})_6$. On strongly heating, these salts yield others of the constitution MSbO_3 , with loss of water. The sparingly soluble *sodium antimonate*, $\text{NaSb}(\text{OH})_6$, is precipitated by addition of the soluble potassium salt to solutions containing sodium ions, for which the latter salt is therefore a test (provided very many other ions are absent). Antimonates are best obtained by dissolving precipitated antimony trisulphide in caustic alkali, and then oxidizing the solution with hydrogen peroxide.

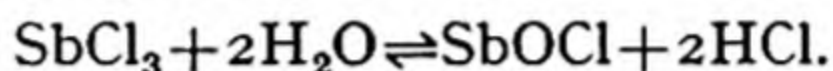
Antimony trichloride, SbCl_3 , is most conveniently prepared by warming the metal in a current of chlorine; once started, the reaction proceeds spontaneously and vigorously. Excess of

chlorine should be avoided, or the product will be contaminated with a little pentachloride.

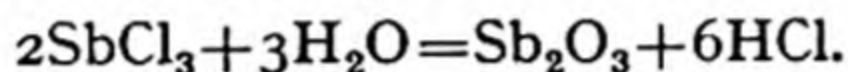
Antimony trichloride may also be prepared by dissolving the sulphide in concentrated hydrochloric acid and evaporating:



It is a colourless, very deliquescent, crystalline solid (M.P. 73° , B.P. 220°), and was formerly known by the 'kitchen name' of *butter of antimony*. It will dissolve to a clear solution in a *small* quantity of water, but on dilution the white oxychloride ('powder of Algaroth') is precipitated:



The precipitate may be re-dissolved by addition of hydrochloric acid, since the above reaction is reversible. Boiling water hydrolyses antimony trichloride completely, to the trioxide:

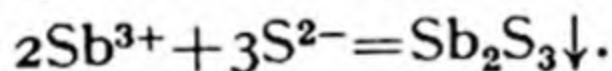


Antimony pentachloride, SbCl_5 , is a colourless liquid made by passing chlorine into the molten trichloride. It dissolves without decomposition in cold water, from which it can be crystallized out as the *monohydrate*, $\text{SbCl}_5 \cdot \text{H}_2\text{O}$. Hot water hydrolyses it to *antimonic acid* (i.e. the hydrated pentoxide).

When heated, antimony pentachloride dissociates (cf. phosphorus pentachloride):

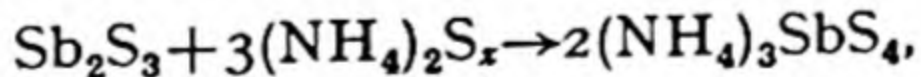


Antimony trisulphide, Sb_2S_3 , which occurs as the black mineral stibnite, is precipitated in an orange-red form when hydrogen sulphide is passed into a solution containing antimonious ions (as in Group II of the analytical tables):

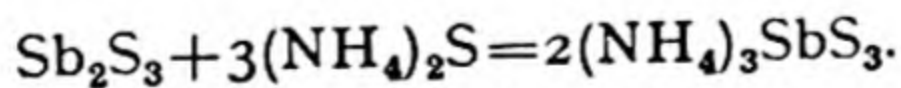


The red form changes to the black when heated to 200° .

Antimony trisulphide is insoluble in dilute hydrochloric acid. It is, however, readily soluble in *yellow* ammonium sulphide, forming the thioantimonate:



and also in *colourless* ammonium sulphide, forming the thioantimonite:

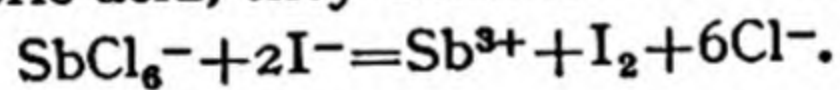


Addition of acid to a solution of the thioantimonite re-precipitates antimony trisulphide, while on acidification of the thioantimonate solution a precipitate of either the pentasulphide, As_2S_5 , or a mixture of the trisulphide and sulphur, is obtained.

Antimony trisulphide is used in pyrotechny, in making matches, and in vulcanizing (red) rubber.

Tests for Antimony.

1. Charcoal block: brittle beads of metallic antimony, soluble in aqua regia.
2. MARSH'S test (p. 479): black stain, insoluble in bleaching-powder solution.
3. Solutions of *antimonious* compounds give with
 - (a) hydrogen sulphide: orange-red precipitate of Sb_2S_3 (see above);
 - (b) excess of water: white precipitate of a basic salt, soluble in hydrochloric acid or tartaric acid;
 - (c) sodium hydroxide: white precipitate of the hydrated trioxide, readily soluble in excess;
 - (d) zinc (in absence of oxidizing agents): black precipitate of metallic antimony.
4. *Antimonic* compounds may be distinguished from antimonious compounds by the fact that, with a solution of potassium iodide and hydrochloric acid, they liberate free iodine:



(Cf. arsenates and phosphates.)

BISMUTH, Bi

Atomic number: 83. *Atomic weight*: 209.0. *Specific gravity*: 9.8.
Melting-point: 271°. *Boiling-point*: 1,560°.

History, Occurrence, and Extraction. Bismuth compounds were known to PARACELSUS and others, from the early sixteenth century onwards, but that bismuth is a distinct chemical element was first shown by GEOFFROY in 1753. Bismuth is found native in Bolivia and certain other localities, and occurs also in the form of its oxide, Bi_2O_3 , *bismuth ochre*, and sulphide, Bi_2S_3 , *bismuth glance*. From ores containing the free element, bismuth is obtained by *liquation*, i.e. by heating the ore until the metal melts and then running it off from the residual rocky matter.

Properties. Bismuth is a soft white metal, and conducts electricity (though not very well). It is unaffected by dry or damp air at ordinary temperatures, but will burn if heated to a high temperature in air or oxygen, forming the trioxide, Bi_2O_3 . It will not dissolve in dilute acids (except nitric acid) but is dissolved by hot concentrated sulphuric acid, yielding bismuth sulphate, $\text{Bi}_2(\text{SO}_4)_3$. Moderately concentrated nitric acid converts it into bismuth nitrate, $\text{Bi}(\text{NO}_3)_3$. Alone among the elements of its group (P, As, Sb, and Bi), bismuth forms no allotropes.

Bismuth is of importance (a) industrially, as a constituent of many fusible alloys (e.g. Rose's alloy and Lipowitz's alloy, p. 420), and (b) medicinally, as a source of many compounds of remedial value.

Compounds. *Bismuth chloride*, BiCl_3 , is a white crystalline solid prepared by synthesis or by dissolving bismuth oxide in concentrated hydrochloric acid: $\text{Bi}_2\text{O}_3 + 6\text{HCl} \rightleftharpoons 2\text{BiCl}_3 + 3\text{H}_2\text{O}$. It is partially hydrolysed by water to the white insoluble oxychloride *bismuthyl chloride*: $\text{BiCl}_3 + \text{H}_2\text{O} \rightleftharpoons \text{BiOCl} + 2\text{HCl}$. *Bismuth trioxide*, Bi_2O_3 , is a yellowish-white basic oxide prepared by heating the nitrate or basic carbonate: $\text{Bi}_2\text{O}_2\text{CO}_3 = \text{Bi}_2\text{O}_3 + \text{CO}_2\uparrow$. *Bismuth nitrate*, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, can be obtained by dissolving the metal, its trioxide, or its basic carbonate, in nitric acid. It cannot be prepared anhydrous, since on heating (or even on standing in a dry atmosphere) it decomposes, forming the basic nitrate $(\text{BiO} \cdot \text{NO}_3)_2 \cdot \text{H}_2\text{O}$ (*bismuthyl nitrate*). Bismuth does not form a normal carbonate, but the *basic carbonate* (*bismuthyl carbonate*), $(\text{BiO})_2\text{CO}_3$, comes down as a white precipitate when a solution of an alkali carbonate is added to a solution of a bismuth salt.

COMPARATIVE EXERCISES

(See p. 427)

1. Make an *outline* comparative table for the series N—P—As—Sb—Bi. This should confine itself to major points, should be of such a length as to be reproducible in writing in half an hour, and should be memorized.

2. Make more detailed comparative tables for (i) nitrogen and phosphorus, (ii) phosphorus and arsenic, and (iii) arsenic, antimony, and bismuth.

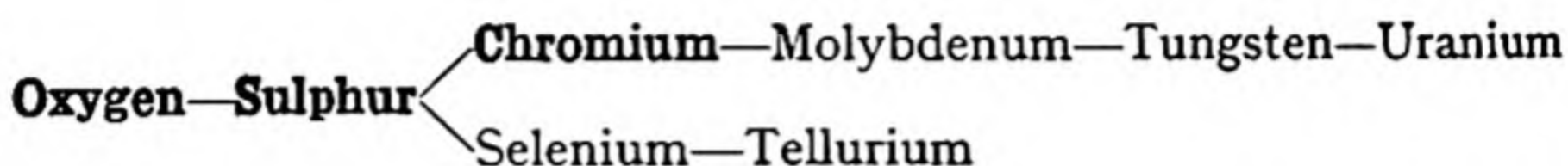
3. Tabulate the resemblances and differences between (i) ammonia and phosphine, (ii) phosphine, arsine, and stibine, (iii) the oxyacids of nitrogen and the oxyacids of phosphorus.

4. Compare and contrast the properties of boron and its compounds with those of silicon and its compounds.

CHAPTER XXIX

GROUP VI

OXYGEN, SULPHUR



The Oxygen Family. The typical elements of Group VI, viz. oxygen and sulphur, closely resemble Sub-group B (selenium and tellurium), but have very little in common with Sub-group A. The elements of this sub-group, however, resemble one another, and also show a similarity to manganese and iron (Chapter XXXI).

OXYGEN, O

Atomic number: 8. *Atomic weight:* 16.000. *Density* ($H=1$): 15.9
Melting-point: -219° . *Boiling-point:* -183° .

History. Oxygen was discovered by SCHEELE in 1772, and independently by PRIESTLEY in 1774 (see p. 8). The name *oxygen* was given to it by LAVOISIER.

Occurrence. Oxygen is the most abundant element in the earth's crust, of which it forms about 50 per cent by weight. Here it is mainly in the form of *silicates* (p. 406) and *carbonates* (p. 386). Oxygen also forms 88.9 per cent by weight of water, and occurs as the free element in the air (21 per cent by volume, 23 per cent by weight).

Industrial Preparation. Pure oxygen is obtained industrially by the electrolysis of water, and as a by-product in the electrolytic manufacture of sodium from fused sodium hydroxide (p. 287). Oxygen of a lower degree of purity is prepared by the fractional distillation of liquid air, a process the principles of which were discussed on p. 62. Air freed from carbon dioxide and moisture is compressed to about 200 atmospheres, and passes into the apparatus shown in Fig. 90 through the pipe D, which branches into a number of smaller pipes, d, at the point where it enters the wider coils C and E. When the pipes d leave C and E, they reunite to form a single pipe, d₁, which is coiled in the vessel B and communicates with the spindle-valve H. On emerging from the valve, the air suddenly expands, and the JOULE-THOMSON cooling effect occurs.

The cooled air is discharged through the rose-ended pipe d_2 into the top of the rectification column A. From A it flows through the outlet pipes C and E which surround the small tubes d, thus cooling the incoming compressed air. The apparatus is enclosed in a suitable casing, and thoroughly lagged with heat-insulating material.

After a time some of the expanded air begins to liquefy, and, dripping from the rose-end of pipe d_2 , trickles down through the rectifying column. Nitrogen, with a boiling-point of -196° , is more volatile than oxygen, so that the liquid gradually becomes richer in oxygen as it flows down the rectifier. This rich oxygen liquid accumulates in vessel B, and is kept boiling by the (comparatively) warm compressed air passing through the coil—which acts as a heat-interchanger—until practically all the nitrogen has been removed and the liquid consists mainly of oxygen (B.P. -183°). Liquid air passing down the column is brought into intimate contact with the gaseous oxygen rising from B, and at each stage some of the oxygen is condensed while some of the nitrogen in the descending liquid is vaporized.

The gas that passes off from the top of the column through the pipe C is mainly nitrogen; through the pipe E, on the other hand, oxygen passes off, and is compressed into cylinders.

This kind of apparatus, though satisfactory on the small scale, involves a loss of about one-third of the oxygen in the air compressed, and where larger quantities of air have to be fractionated (e.g. to obtain argon, krypton, neon, etc.) the design of the plant is much more complex. The general principles involved are, however, similar to those described.

Laboratory Preparation. There are many ways in which oxygen can be prepared in the laboratory. That most commonly employed is to heat potassium chlorate, using manganese dioxide as a catalyst:

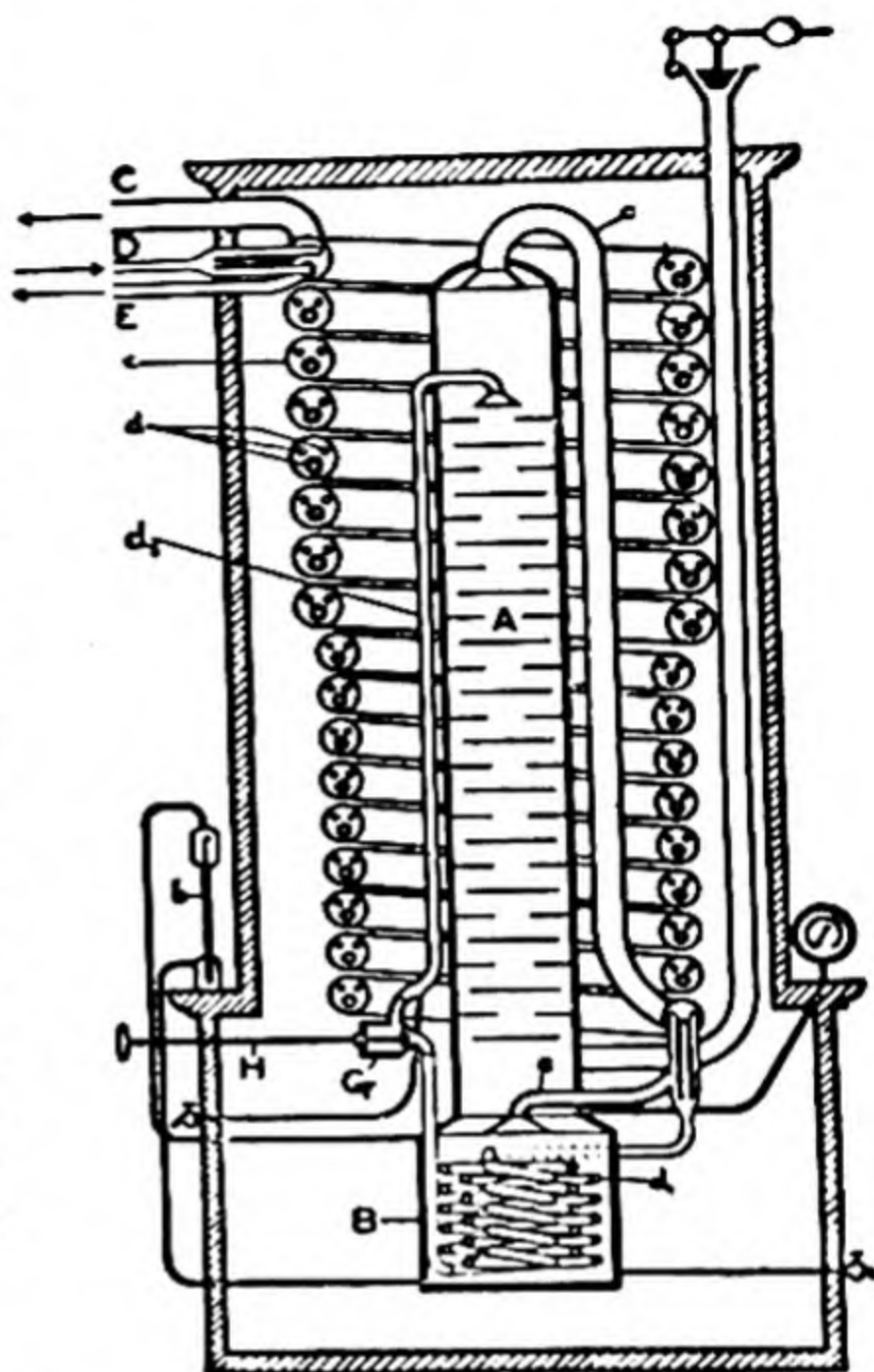
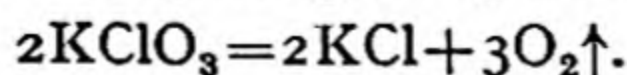
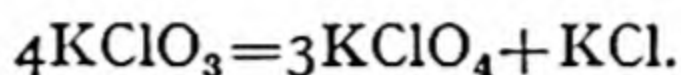


FIG. 90. LIQUID OXYGEN MACHINE (Diagrammatic)

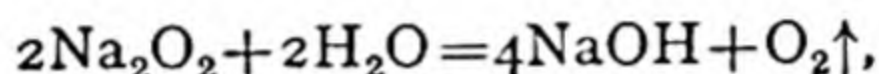
If potassium chlorate is heated alone, it melts at 370° but solidifies again at a slightly higher temperature, owing to the formation of *potassium perchlorate*, KClO_4 , which has a higher melting-point than the chlorate:



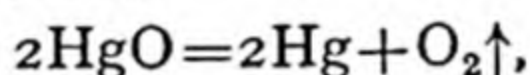
At about 400° , the perchlorate decomposes into the chloride and oxygen: $\text{KClO}_4 = \text{KCl} + 2\text{O}_2\uparrow$, so that the net result of heating the chlorate is the same whether a catalyst is present or not. In the presence of manganese dioxide (or other catalyst such as ferric oxide or cobaltic oxide), potassium perchlorate is not formed, and the chlorate decomposes direct into the chloride and oxygen at temperatures below its melting-point.

The gas may be dried with calcium chloride and collected over mercury. If it is not required dry it may be collected over water.

Oxygen may also be prepared by dropping water on to sodium peroxide:



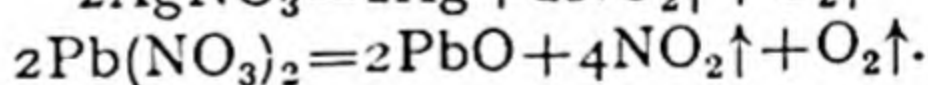
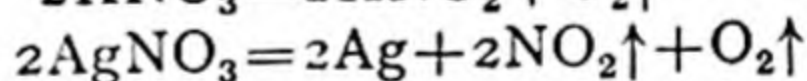
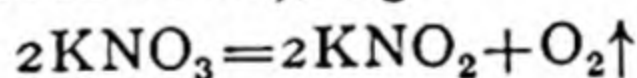
or by heating mercuric oxide:



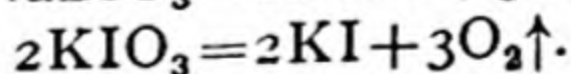
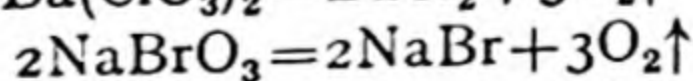
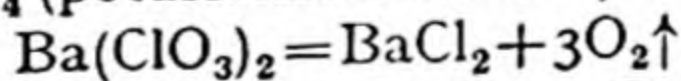
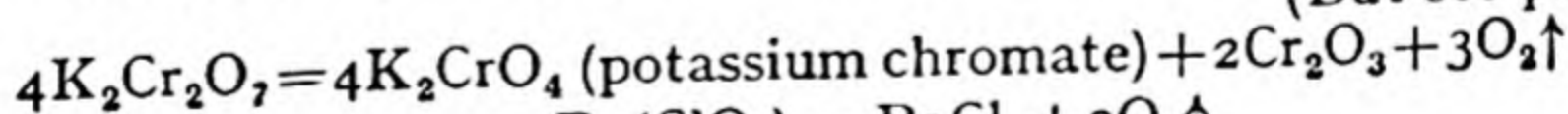
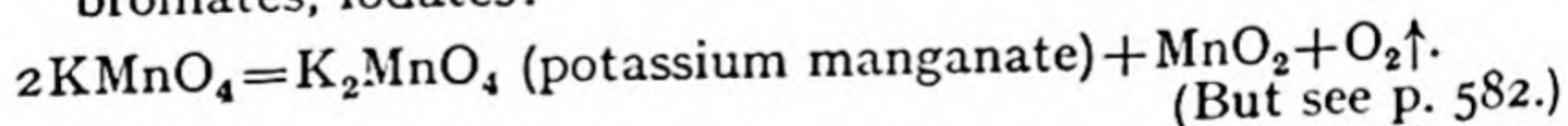
though this last method has nothing more to recommend it than its historical interest.

Various other reactions in which oxygen is liberated are:

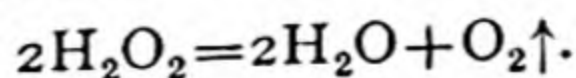
- (i) The electrolysis of water (which must contain an electrolyte). The oxygen is liberated at the anode.
- (ii) The action of heat on nitrates (except ammonium nitrate which yields nitrous oxide), e.g.:



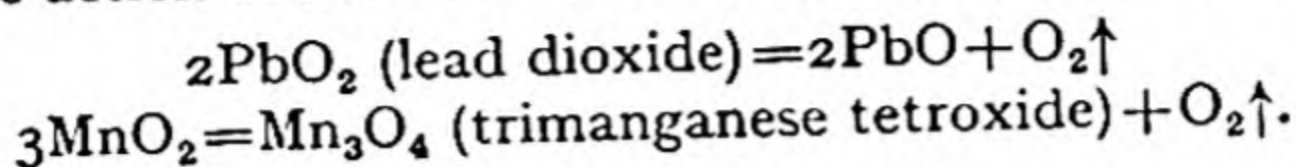
- (iii) The action of heat on permanganates, dichromates, chlorates, bromates, iodates:



- (iv) The catalytic decomposition of hydrogen peroxide, e.g. in the presence of platinum black:



(v) The action of heat on various higher metallic oxides, e.g.:



Properties. Oxygen is a colourless, odourless, and tasteless gas which can be condensed to a pale blue liquid (B.P. -183°), and frozen to a crystalline solid of similar colour (M.P. -219°). Liquid oxygen is strongly magnetic, and will adhere to the poles of a powerful electromagnet.

Oxygen is slightly soluble in water, 1 c.c. of which at 0° will dissolve 0.0489 c.c. of the gas measured at N.T.P. Small as this solubility is, it is nevertheless the condition of the existence of aquatic life. Oxygen is also soluble in certain molten metals, such as silver, but is released when the metal solidifies (see p. 324).

Under appropriate conditions oxygen will combine with all other elements, except the inert gases, to form compounds known as *oxides*, several of which are formed by many elements.

The total number of oxides therefore exceeds that of any other type of inorganic compound, and since their chemical behaviour is also very diversified, it becomes necessary to seek a basis for their classification. Many oxides are essentially *basic* in function: that is, with acids they yield a salt and water as sole products; the element other than oxygen enters the *cation* of the salt. Other oxides are *acidic* and yield a salt and water as sole products in action with alkalis; the element other than oxygen enters the *anion* of the salt. A considerable number of oxides exhibit each of these characteristics in appropriate conditions, and are termed *amphoteric*. It is convenient to use the terms *higher* and *lower oxide* to connote a higher or lower proportion of oxygen respectively.

(A) OXIDES CONTAINING DISCRETE OXYGEN ATOMS OR OXYGEN IONS (O^{2-}).

(1) *Basic oxides*: Non-volatile oxides of composition M_2O , MO , M_2O_3 (exception B_2O_3 , which is wholly acidic; ZnO , Al_2O_3 , SnO , and PbO are amphoteric).

(2) *Acidic oxides*:

(a) Volatile oxides M_2O_3 and higher.

(b) Non-volatile oxides MO_2 and higher.

(Exceptions: CeO_2 , ZrO_2 , ThO_2 are basic; TiO_2 is feebly basic, but principally acidic.)

All basic oxides are metallic: no element could qualify chemically as a metal unless it formed at least one basic oxide. Basic and acidic oxides if soluble in water yield alkaline or acid solutions respectively. The distinction between volatile and non-volatile is

broadly that between ionic and covalent oxides, but there are some notable exceptions: among basic (or amphoteric) oxides the following are covalent in constitution: Cu_2O , Ag_2O , CuO , ZnO , HgO , SnO , and PbO . The class of non-volatile acidic oxides contains B_2O_3 and SiO_2 , both of which are covalent.

In the case of those metals which have many oxides (e.g. manganese and chromium), the lowest oxides are basic and usually ionic (CrO , MnO , Cr_2O_3 , Mn_2O_3) and the highest oxides strongly acidic and covalent (Mn_2O_7 , CrO_3). The lowest metallic oxides having an acidic function are dioxides such as TiO_2 , MnO_2 , and PbO_2 , all of which are ionic, and indifferent to aqueous alkali; their necessarily very feeble acidity is only evinced on fusion with alkali, when titanate (TiO_3^{2-}), manganite, (MnO_3^{2-}) and plumbate (PbO_3^{2-}) are formed.

(3) *Mixed oxides:*

(a) Fe_3O_4 , $\text{Li}_2\text{Fe}_2\text{O}_4$, MgAl_2O_4 , CaTiO_3 . The constituent oxides in these examples, viz. FeO , Fe_2O_3 ; Li_2O , Fe_2O_3 ; MgO , Al_2O_3 ; CaO , TiO_2 , are all ionic compounds and the mixed oxides exist because it is possible to build a stable crystal structure in which the cations jointly balance the charges upon the oxygen anions, e.g. $(\text{Mg}^{2+}\text{Al}_2^{3+})\text{O}_4^{2-}$ and $(\text{Ca}^{2+}\text{Ti}^{4+})\text{O}_3^{2-}$. Terms such as 'lithium ferrite,' 'magnesium aluminate,' etc., are therefore misnomers. Titanium dioxide does, however, form a true titanate, with anion TiO_3^{2-} , on fusion with potassium hydroxide (see above).

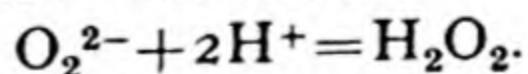
(b) Pb_3O_4 , Sb_2O_4 . In these examples the constituents are PbO , PbO_2 , and Sb_2O_3 , Sb_2O_5 , of which only PbO_2 is ionic. In the crystal structure of minium the covalent character of PbO and the ionic structure of PbO_2 are both preserved: the structure of antimony tetroxide awaits investigation.

(4) *Neutral oxides:* This is a small class comprising the volatile oxides H_2O , N_2O , CO , and NO .

(B) OXIDES CONTAINING A COVALENT LINK BETWEEN OXYGEN ATOMS.

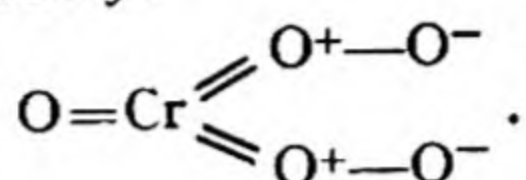
(I) *Peroxides:*

(a) *Ionic peroxides* contain the anion $(\bar{\text{O}}-\bar{\text{O}})^{2-}$, and yield hydrogen peroxide with acids:



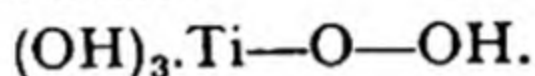
They are formed only by the alkali and alkaline earth metals, well-known examples being Na_2O_2 and BaO_2 , both of which are colourless when pure.

- (b) *Covalent* peroxides contain the bivalent group $=\overset{+}{\text{O}}-\overset{-}{\text{O}}$ (cf. ozone, p. 120). The best known example is CrO_5 , the blue compound produced when hydrogen peroxide is added to acidified dichromate solution; this reaction is used as a test for either reagent. The structural formula of CrO_5 is very probably:



Hydrogen peroxide, H_2O_2 , is the only (inorganic) peroxide containing the bivalent group $-\text{O}-\text{O}-$.

- (c) *Hydro-peroxides*, although not strictly oxides, are very closely related to the covalent peroxides. They contain the univalent group $-\text{O}-\text{OH}$. Addition of hydrogen peroxide and alkali to a solution containing dissolved titanium produces a deep orange precipitate or coloration due to the hydro-peroxide:



The reaction is used as a delicate test for either reagent.

- (2) *Superoxides*: These ionic oxides, all deep yellow in colour, contain the singly charged anion O_2^- , and are formed only by the alkali-metals, with lithium excepted. With acids they yield hydrogen peroxide and oxygen. Examples are NaO_2 and KO_2 . Technical sodium peroxide contains up to 10 per cent of NaO_2 , which gives the peroxide its pale yellow colour.

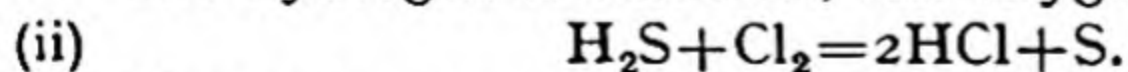
Oxidation and Reduction. Oxidation in the narrow sense signifies the addition of oxygen to a substance, or the removal of hydrogen from it. In a wider sense, oxidation is taken to imply (a) an increase in the proportion of electronegative constituent of a substance, whatever the nature of this constituent, or (b) the removal of electrons from a substance.

Reduction is the reverse of oxidation, and since the two processes are complementary one never takes place without the other.

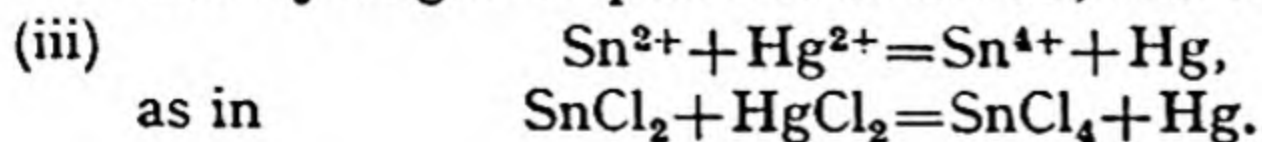
Examples:



The hydrogen is oxidized; the oxygen is reduced.



The hydrogen sulphide is oxidized; the chlorine is reduced.



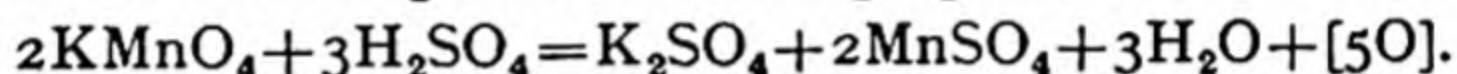
The stannous ion gives up two electrons to the mercuric ion; hence the stannous ion is oxidized and the mercuric ion reduced.

Common *oxidizing agents* are oxygen, ozone, hydrogen peroxide, chlorates, nitrates, permanganates, dichromates, chlorine.

Common *reducing agents* are hydrogen, carbon, carbon monoxide, hydrogen sulphide, sulphur dioxide, stannous chloride.

Both oxidation and reduction can be effected electrolytically.

In an oxidizing agent which contains oxygen, not all the oxygen content is necessarily employed during oxidation. That part of it which is so employed is known as *available oxygen*. For example, in oxidations carried out with hydrogen peroxide, only one of the two oxygen atoms effects oxidation: $\text{H}_2\text{O}_2 = \text{H}_2\text{O} + [\text{O}]$; hence 34 gm. of hydrogen peroxide contain 16 gm. of available oxygen. Similarly, potassium permanganate in dilute sulphuric acid solution behaves as follows when acting as an oxidizing agent:



Hence 2 G.F.W. (316 gm.) of potassium permanganate contain $5 \times 16 (=80)$ gm. of available oxygen.

A quantitative treatment of oxidation-reduction processes (redox reactions) is given in Chapter XVIII, pp. 250–256.

Atomic Oxygen. By passing oxygen at low pressure (1 mm.) through a silent electric discharge, many of the molecules are split up into single atoms; and although these quickly recombine to form the ordinary diatomic molecules, some of the properties of atomic oxygen have been studied. It will, for instance, decompose hydrocarbons, the reactions being accompanied by an intense blue chemiluminescence, and will melt platinum owing to the great heat evolved when the atoms recombine—a reaction strongly catalysed on the surface of the metal.

THE ATMOSPHERE

The air is a complex mixture of gases, the chief of which, together with the proportions by volume in which they occur in average London air, are shown below:

Gas	Proportion by Volume, per cent
Nitrogen	77.32
Oxygen	20.80
Water-vapour	0.92
Carbon dioxide	0.03
Argon	0.932
Neon	0.0015
Helium	0.0005
Krypton	0.000005
Xenon	0.0000006

Air a Mixture. That the nitrogen and oxygen, which form the bulk of the atmosphere, are mixed and not combined is shown by the facts that:

- (a) The proportion of oxygen to nitrogen, though nearly constant, has been reported to vary slightly from place to place and time to time.
- (b) The composition by weight does not correspond to any reasonable chemical formula. The nearest approximate formula, $N_{55}O_{14}$, would require a vapour density enormously greater than the observed value of 14.4.
- (c) The nitrogen and oxygen can be separated by mechanical means, e.g. fractional solution or distillation.

Composition of Dry Air. The proportion by weight of oxygen in dry air, free from carbon dioxide, may be determined by passing air through soda-lime (to remove CO_2) and concentrated sulphuric acid (to dry it), and then over heated copper, which extracts the oxygen as cupric oxide. The residual gas passes on into a previously evacuated, weighed flask of suitable dimensions. From the difference in weight of the copper and cupric oxide, the weight of oxygen is obtained, while the increase in weight of the flask gives the weight of other gases. An average result is oxygen 23.2 per cent. [Of the remaining 76.8 per cent, about 1.3 is argon, etc., so that the true nitrogen/oxygen ratio is 75.5/23.2.]

The volumetric estimation may be carried out by exploding air with excess of hydrogen, when one-third of the diminution in volume represents the volume of oxygen in the air taken. Alternatively the oxygen may be absorbed in alkaline pyrogallol, or made to combine with a copper wire, heated electrically. In these methods, the residual gas is a mixture of nitrogen with the rare gases.

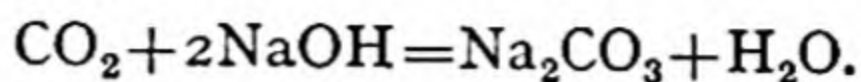
The proportion of *carbon dioxide* in the air may be determined gravimetrically by drawing a known volume of air through concentrated sulphuric acid tubes (to remove moisture) and then through weighed potash-bulbs, the increase in weight of which gives the weight of carbon dioxide in the volume of air employed. A rapid volumetric method, due to HALDANE, is to enclose air in a large globe of known capacity, which communicates with a narrow-bore graduated U-tube containing caustic potash solution. When the carbon dioxide has been absorbed, the decrease in volume can be read off directly, after levelling.

Extraction of Gases from Air. Specimens of water, carbon dioxide, oxygen, and nitrogen may be extracted from air as follows:

Water. Draw a current of air over silica gel (p. 261) for some hours. Heat the silica gel in a distillation apparatus and collect the distillate of water.

Carbon dioxide. Draw a current of air through sodium hydroxide

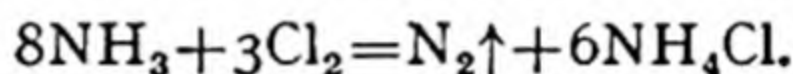
solution for some hours, when sodium carbonate will be formed in solution:



Add dilute sulphuric acid and collect the carbon dioxide evolved.

Oxygen. Draw a current of air through soda-lime and concentrated sulphuric acid and then over heated copper, until a suitable quantity of cupric oxide is formed. Heat this in a current of hydrogen, and condense the water so produced. Add a little common salt, and electrolyse the solution. Oxygen is given off at the anode.

Nitrogen. Remove from air (a) water-vapour, (b) carbon dioxide, and (c) oxygen by the method just described. Pass the residual gas (nitrogen and rare gases) slowly over heated magnesium, to form magnesium nitride, Mg_3N_2 . Add water to this, and dissolve in water the ammonia evolved. Pass chlorine into the ammonia solution:



OZONE, O_3

History. In 1785 the Dutch scientist, MARTIN VAN MARUM (1750–1837), constructed a large frictional-electricity machine, and noticed a penetrating odour when it was in operation. In 1839 the Swiss chemist SCHÖNBEIN (discoverer of gun-cotton and collodion) showed that this odour was due to a definite substance, which he appropriately named ozone (Greek: *ozein*, to smell). That ozone is an allotrope, O_3 , of oxygen was demonstrated by J. SORET in 1866.

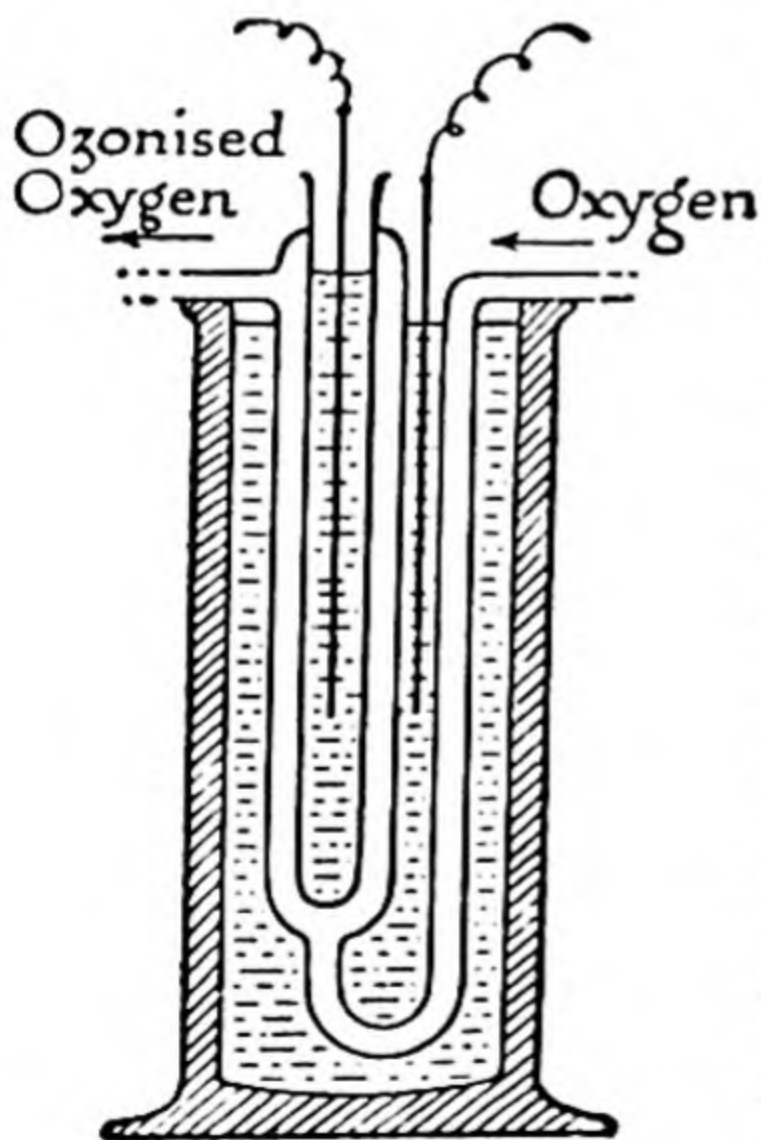
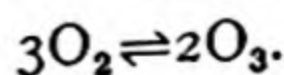


FIG. 91.

A LABORATORY OZONIZER

Preparation. Oxygen may be partly converted into ozone by subjecting it to a silent electric discharge. Many types of ozonizer are in use, a simple form being shown in Fig. 91. A double tube is placed in a jar of dilute sulphuric acid, with which the inner tube is also filled. By means of platinum wires dipping into the acid, a silent discharge from an induction coil is passed across the space through which the current of oxygen flows. The gas that leaves the ozonizer consists of some 10 per cent of ozone and 90 per cent of unchanged oxygen:



In industrial ozonizers the discharge is made to pass between sheets of wire gauze protected by glass plates.

Ozone may be prepared in greater concentration by the electrolysis of cold aqueous sulphuric acid, using a minute smooth platinum anode; the gas evolved contains 20–30 per cent of ozone.

Ozonized oxygen is obtained in many chemical reactions, e.g. (a) when fluorine decomposes water (p. 540), (b) when moderately concentrated nitric acid is heated with ammonium persulphate (p. 536), and (c) by the slow oxidation of phosphorus. It is also formed when oxygen is exposed to ultra-violet light (as the nose of any one who has had ultra-violet treatment will have testified). This is the reason why the upper atmosphere, at a height of about 25 kilometres, contains large quantities of it. In the lower atmosphere there are but the merest traces of ozone.

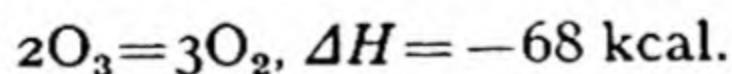
Pure ozone is obtained by liquefying ozonized oxygen and fractionally distilling the liquid. Oxygen boils at -183° and ozone some 70° higher, so that an effective separation can be made.

Properties. Ozone is a pale blue gas, which at low temperatures condenses to a deep indigo blue liquid (B.P. -112°). The liquid on further cooling solidifies to a deep violet crystalline mass (M.P. -250°).

Liquid ozone is extremely explosive unless perfectly pure, but may be vaporized without decomposition if due care is taken. The vapour density of the gas so obtained is 24, which shows that the ozone molecule is O_3 .

Ozone is a poisonous gas, but since it rapidly destroys most of the organic compounds which impart a bad smell to crowded haunts of humanity, it is used to freshen the atmosphere of theatres, concert halls, underground railways, and the like. It also has a powerful germicidal action, but to be of much use in this way considerably higher concentrations of it are necessary than are suitable for air-conditioning. Drinking-water is frequently sterilized with ozone, as are surgical instruments.

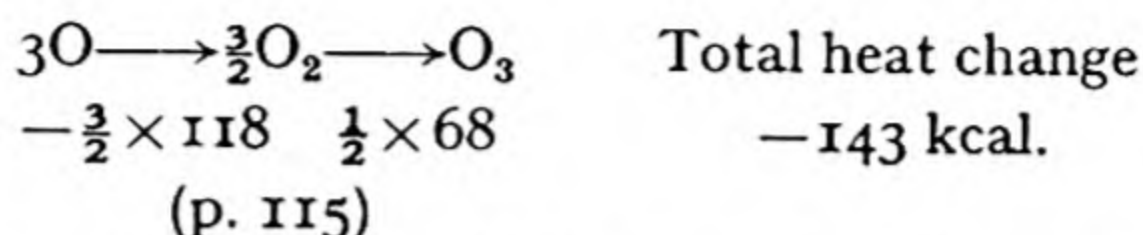
When ozonized oxygen is heated to about 280° – 300° , the ozone is rapidly reconverted into oxygen, with evolution of heat:



Since ozone is an endothermic substance, the proportion of it in equilibrium with oxygen, $3O_2 \rightleftharpoons 2O_3$, rises with rise of temperature; at ordinary temperatures, however, the *actual* proportion of ozone in ozonized oxygen very greatly exceeds the *equilibrium* proportion,* and gentle heat is sufficient to decompose the excess.

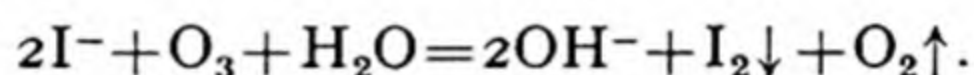
* Which is negligibly small, even at 300° .

In respect to its formation from oxygen *atoms*, ozone is strongly exothermic:

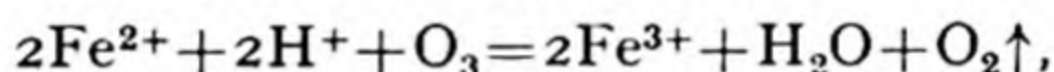


Ozone is rather more soluble in water than oxygen. It also dissolves readily in organic liquids containing one or more ethylenic linkages, combining with them to form *ozonides*, e.g. benzene ozonide, $\text{C}_6\text{H}_6(\text{O}_3)_3$. Rubber contains many ethylenic linkages, and the destructive effect of ozone upon rubber tubing is thus easily understood.

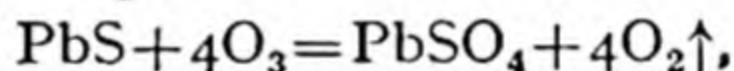
Ozone is a powerful oxidizing agent. Even at ordinary temperatures it oxidizes a mercury surface, and so causes the mercury to 'tail,' or stick to glass. It will also oxidize silver to a mixture of oxides, Ag_2O , AgO , and Ag_2O_3 , and liberates iodine from potassium iodide solution:



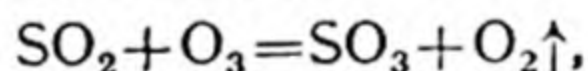
Ozone oxidizes ferrous salts to ferric salts in acid solution:



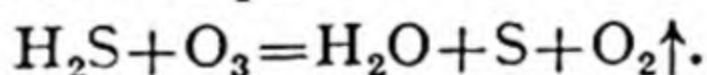
lead sulphide to lead sulphate:



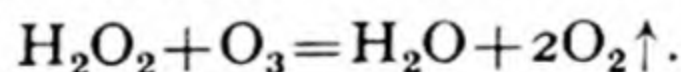
sulphur dioxide to sulphur trioxide:



and hydrogen sulphide to sulphur:



Hydrogen peroxide is oxidized to water and oxygen:



For discussion of the structure of ozone, see Chapter X, p. 120.

Tests for Ozone.

1. The 'tailing' of mercury.
2. Liberation of iodine from potassium iodide solution—though this is brought about by many other oxidizing agents.
3. Ozone has no effect upon potassium permanganate solution (distinction from hydrogen peroxide, p. 509).
4. Ozone gives a bluish-violet colour to a solution of 'tetra-base' (tetramethyl-p-p'-diaminodiphenyl-methane).
5. The smell of ozone is characteristic (unless the gas is too dilute, when it may be mistaken for chlorine).
6. When ozone oxidizes nitric oxide, a luminescence is produced.

WATER

Occurrence. The plight of the Ancient Mariner, who saw 'Water, water, everywhere, Nor any drop to drink,' was occasioned by the fact that, while water is the most abundant of all compounds, it is also the best solvent and so never occurs pure in nature. The principal types of natural 'water' (i.e. natural aqueous solutions) are:

(i) *Rain-water.* This is natural distilled water and contains as impurity only the gases it has dissolved from the air (though near the sea it may contain appreciable quantities of salt, from the sea spray, and near towns it collects suspended solid particles of soot, etc.).

(ii) *River-water.* The water of rivers contains differing quantities and kinds of dissolved matter, according to the nature of the strata over and between which it flows. The Thames, for example, which flows through limestone districts, contains much more matter in solution than the (Scottish) Dee, which flows over granite. Rivers are also frequently contaminated with sewage and with factory waste, while tidal rivers are twice a day salty at some considerable distance from their mouths, owing to the influx of the tide.

(iii) *Spring-water and deep well-water.* During its passage through the earth, from the surface to an impervious stratum, rain-water dissolves mineral substances, e.g. chalk. At the same time, this percolation removes suspended impurities, such as bacteria, so that the water is usually potable.

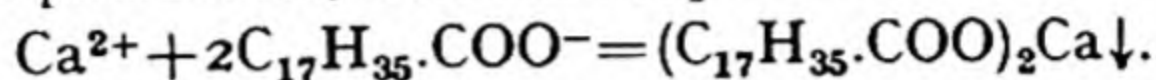
(iv) *Lake-water.* The nature of lake-water, like that of river-water, depends upon the nature of the strata over which it flowed on its way to the lake. In limestone districts it contains calcium bicarbonate, while in granite regions the amount of dissolved solid matter may be very small.

(v) *Sea-water.* Sea-water contains the chlorides, bromides, iodides, sulphates, bicarbonates, and other salts of sodium, potassium, magnesium, calcium, and other metals. Indeed, acting as the world's scavenger, it has in the course of ages collected an amazing variety of solutes—even gold. A litre of sea-water yields, on an average, 36 gm. of solid residue on evaporation. Of this about 26 gm. is common salt.

(vi) *Mineral waters.* The waters of certain springs—for example, those at Bath, Cheltenham, Harrogate, Leamington, Vichy, Aix, Evian, Carlsbad, Bad Ems, and Wiesbaden—contain various salts (e.g. magnesium sulphate) and gases (e.g. radon, hydrogen sulphide) that render them suitable for medicinal purposes. The more unpleasantly they taste or smell, the more popular they appear to be. They are known as 'mineral waters,' a name also applied (frequently in its ignorantly abridged form of 'minerals') to soda-water and

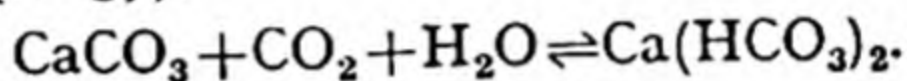
other artificial beverages charged with carbon dioxide, since these were first prepared (by PRIESTLEY) as imitations of the natural mineral waters.

Hardness of Water. Water which will not lather immediately with ordinary soap (i.e. sodium stearate, $C_{17}H_{35}.COONa$, or sodium palmitate, $C_{15}H_{31}.COONa$) is said to be *hard*. It contains the ions of metals—chiefly calcium and magnesium—which form insoluble stearates and palmitates, and the soap is therefore destroyed:



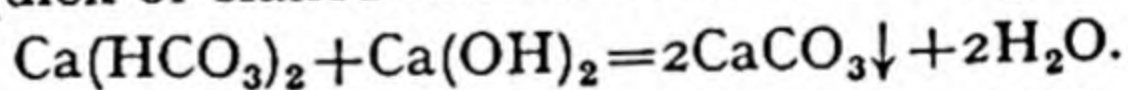
Continued addition of soap will of course at length soften the water, but the process is tedious and wasteful.

Water commonly acquires hardness either by flowing over deposits of gypsum ($CaSO_4.2H_2O$), which is slightly soluble, or over limestone or chalk, $CaCO_3$. Calcium carbonate is practically insoluble in pure water, but water containing dissolved carbon dioxide (e.g. from the atmosphere and soil atmosphere) converts it into the soluble bicarbonate (see p. 237).

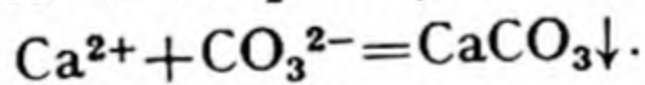


Hardness caused by the presence of calcium (magnesium, etc.) sulphate is described as 'permanent,' since it cannot be removed by boiling; that caused by calcium (magnesium, etc.) bicarbonate is said to be 'temporary,' since the bicarbonate is reconverted into the insoluble carbonate on heating, and the hardness is lost.

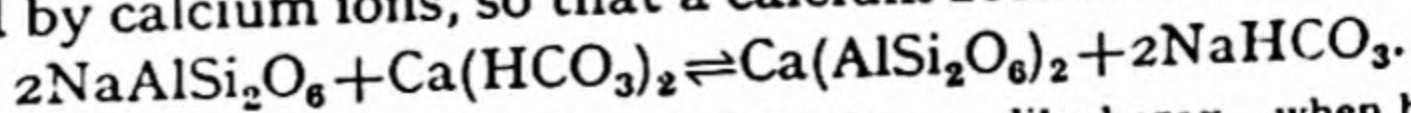
Temporary hardness may be removed by adding the correct quantity of quick or slaked lime to react according to the equation:



Permanent hardness may be removed by addition of sodium carbonate—which removes temporary hardness as well:

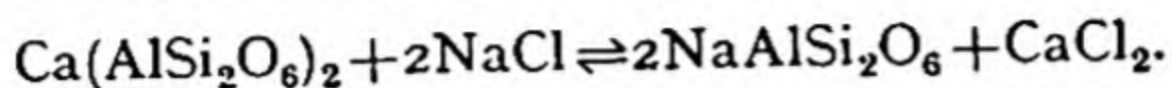


Both permanently hard water and temporarily hard water may be softened by the *zeolite** or 'base-exchange' method. Zeolites are the naturally occurring forms of sodium aluminosilicates, e.g. $Na(AlSi_2O_6)$, or *analcite*; for water-softening purposes similar substances† are prepared artificially. The anionic or $AlSi_2O_6^{-}$ parts of the compounds appear to form a complex open-work structure, in the tortuous passages of which the sodium ions are situated. When hard water is passed through a zeolite, the sodium ions are replaced by calcium ions, so that a calcium zeolite is formed:



* Greek, 'boiling stone,' because a zeolite froths up—like borax—when heated.
† e.g. that sold under the trade name of 'Permutit.'

The calcium is therefore retained, and the issuing water is soft. The reaction is, however, reversible, so that the original sodium zeolite may be recovered when required, by the addition of strong brine to the calcium zeolite:



The calcium chloride solution is then run off to waste, and the softener is ready for use again.

Another useful water-softener is *sodium polymetaphosphate*, which is described on p. 473. This not only removes calcium ions from the water, but will also dissolve the rocky deposits of calcium carbonate and sulphate formed in boilers where hard water has been used. By both polymetaphosphate and zeolites calcium ions are 'sequestered' within the framework of very large anions.

The hardness of a given specimen of water is estimated by titration with a standard solution of soap in dilute alcohol, the end-point being the formation, on shaking, of a lather that lasts for 3 minutes. One degree of hardness corresponds to the presence of 1 gm. of calcium carbonate, or its equivalent (i.e. 0.4 gm. calcium ion, Ca^{2+}), in 100 litres of water. The soap solution itself is standardized against a standard solution of calcium chloride, made by dissolving 1.000 gm. of Iceland spar (CaCO_3) in the least possible quantity of dilute hydrochloric acid and diluting to one litre with distilled water.

For laundry, hot-water circulation, and boiler purposes, soft water is obviously preferable. For drinking purposes, water should not be entirely soft since it is insipid, lacks the calcium salts necessary to bodily health, and dissolves lead, which is a cumulative poison. Hard water coats lead pipes with a film of lead carbonate or sulphate (or both), which prevents further action.

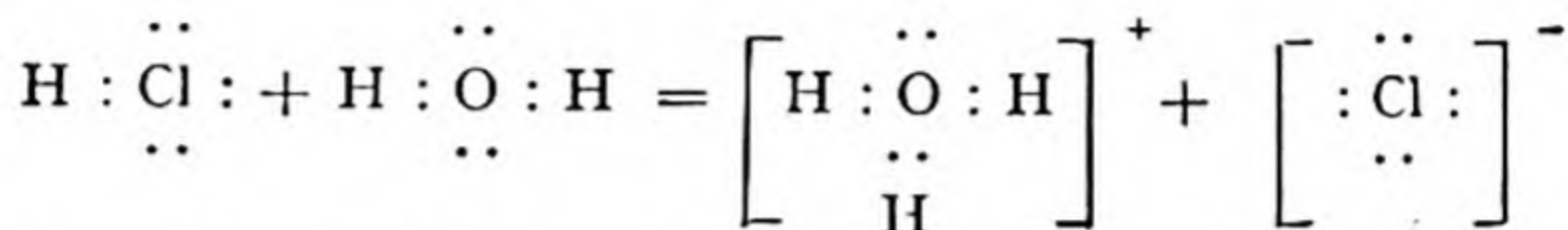
NOTE. The difficulty of obtaining a lather with soap in sea-water is due to the magnesium and calcium ions it contains.

Purification of Water. The purification of water is best effected by distillation. For the preparation of chemically pure water, see p. 216.

Properties of Water. Water is an odourless and tasteless liquid which in small quantities appears to be without colour, though large masses are blue or green. At 760 mm. it melts at 0° and boils at 100° (the thermometric 'fixed points'). Its density at 4° is exactly 1 gm. per c.c., since the gram is defined as the weight of 1 c.c. of water at this temperature. In many ways water has unusual and unexpected properties; thus it boils about 162° higher than its analogue hydrogen sulphide, increases in density from 0° to 4° , and possesses abnormally high specific and latent heats (p. 118).

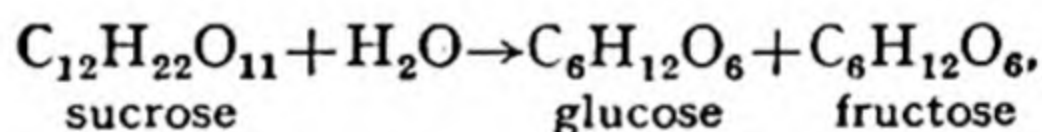
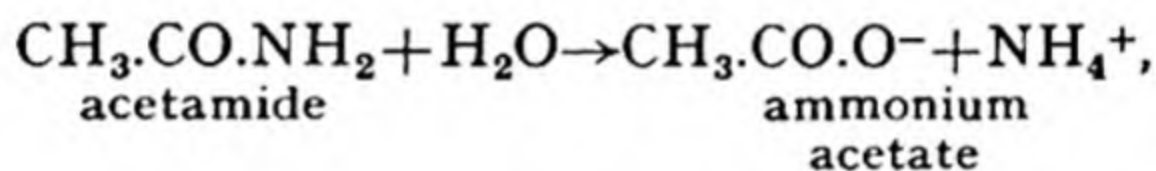
Water is an exceedingly good solvent, dissolving certain elements (e.g. chlorine, bromine, oxygen), most electrolytes, and many covalent compounds (e.g. alcohol, urea, sugars). It is also the best 'ionizing' solvent, a fact connected with its high dielectric constant and with the ability of its molecule to 'donate' and share electrons. Thus when the covalent compound hydrogen chloride

$\text{H} : \overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{Cl}}} :$ is dissolved in water $\text{H} : \overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}} : \text{H}$, the following reaction occurs:



and a solution of highly ionized hydrochloric acid is formed (cf. p. 109).

Water is very slightly ionized (p. 216), but the fact that it is ionizable is of considerable importance, as was explained in Chapter XVII, pp. 216-17. Water will hydrolyse many organic compounds, e.g.:



though in general a catalyst is necessary to make the reaction proceed conveniently quickly (Chapter XV, p. 188).

Water of crystallization. On separation from aqueous solution, many salts form crystals containing molecules of the salt combined with molecules of water. This water is known as water of crystallization or hydration, and salts containing it are called 'hydrated salts' or 'hydrates.' Crystalline hydrates are also formed by many other substances, e.g. oxalic acid, sodium hydroxide, glucose, methane, and the rare gases.

The water molecules in a hydrate are not necessarily all bound in the same way. Thus BEEVERS and LIPSON, using X-ray methods, have shown that in copper sulphate crystals, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, four out of every five water molecules are arranged in a square surrounding a copper ion, while the fifth occupies an entirely different kind of position. It forms 'hydrogen bonds' (p. 118) between an oxygen atom in the sulphate anion, SO_4^{2-} , and a water molecule bound to the cation Cu^{2+} . Many sulphates of bivalent metals are heptahydrates, e.g. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. In these, six molecules of water surround the cation at the corners of an octahedron, and the seventh

forms hydrogen bonds as in copper sulphate. Such bonds necessitate an oxy-anion: consequently magnesium chloride crystallizes as a *hexahydrate*, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$.

The phenomena of *deliquescence* and *efflorescence* were considered on p. 171.

Volumetric Composition of Water. In 1776 MACQUER noticed that a cold object held in the flame of burning hydrogen became covered with drops of water. Five years later PRIESTLEY observed that, after the explosion of mixtures of hydrogen and oxygen, the interior of the vessel was damp. Shortly afterwards, CAVENDISH found that when 2 volumes of hydrogen were exploded with 1 volume of oxygen, all the gas disappeared and water was formed. He did not, however, consider that this result proved water to be a compound of hydrogen and oxygen, for he regarded hydrogen as *water-plus-phlogiston* and oxygen as *water-minus-phlogiston*. On exploding the gases in the right proportion, the extra phlogiston of the hydrogen was transferred to the oxygen, and so each gas was *individually* converted into water. It was LAVOISIER who, in 1784, first expressed the opinion that water is in reality hydrogen oxide.

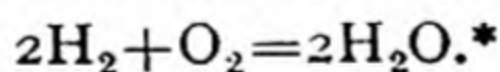
Exact measurements of the volume-ratio in which hydrogen and oxygen combine were made by SCOTT in 1893 and BURT and EDGAR in 1915. Scott prepared pure hydrogen by passing steam over sodium, and pure oxygen by heating pure silver oxide (precipitated from silver nitrate solution by potassium hydroxide). His results gave the volume-ratio:

Hydrogen : oxygen = 200.285 : 100.

Burt and Edgar's figures agreed very closely; they obtained the volume-ratio:

Hydrogen : oxygen = 200.288 : 100.

As a laboratory experiment, the volumetric composition of steam may be found by exploding 2 volumes of hydrogen with 1 volume of oxygen in the close limb of a U-shaped eudiometer, this limb being kept at 130° by enclosing it in a glass jacket through which the vapour of boiling amyl alcohol is passed. It is proved that no uncombined hydrogen or oxygen is left, and that the volume of the steam formed is equal to that of the hydrogen used; hence by Avogadro's principle the formula of steam is H_2O :



* The reaction described wittily—and with a musical accompaniment—in Professor J. READ's charming book *Prelude to Chemistry* (London, G. Bell & Sons Ltd.), which every chemist, and every aspiring chemist, should possess:

'Aère cum crasso tenuis componitur aère;

Adde Iouis fulmen, fit sonus, unda manet.

With a dense gas a thin gas is mixed; pass the electric spark, and pop! you have water.'

Gravimetric Composition of Water. In 1842 DUMAS carried out an elaborate determination of the ratio by weight in which oxygen and hydrogen combine to form water. The principle of his method was to pass hydrogen over heated cupric oxide, and to find (a) the loss in weight of the cupric oxide and (b) the weight of water formed. Unfortunately, although he took every precaution he could think of, there were too many sources of error left unperceived for his figures to be very accurate. He obtained the weight-ratio:

$$\text{Hydrogen : oxygen} = 1.00 : 7.98.$$

Direct synthesis, a much better method, was employed by MORLEY in 1895. The apparatus he used is shown diagrammatically in

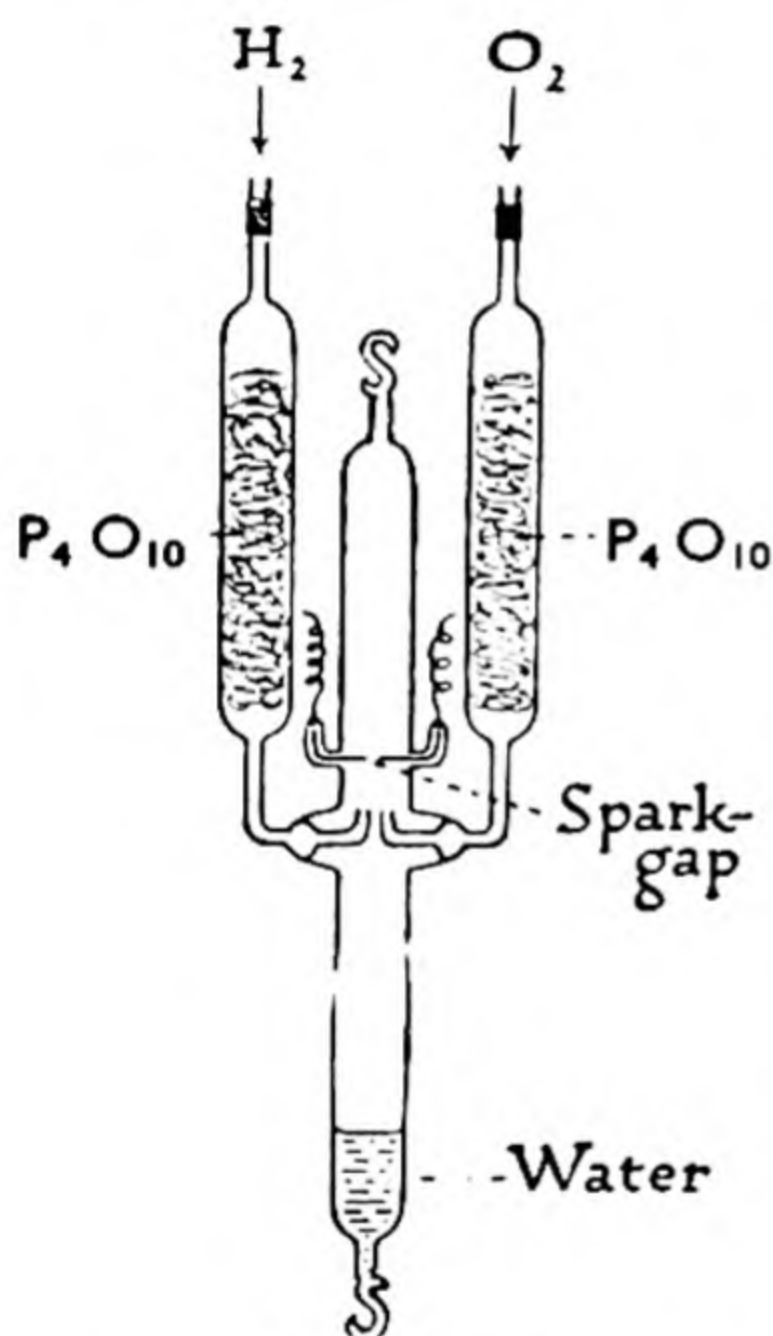


FIG. 92.

MORLEY'S APPARATUS

Fig. 92. Pure hydrogen was prepared by the electrolysis of pure dilute sulphuric acid, and was passed through an almost saturated solution of potassium hydroxide (to remove any possible sulphur dioxide), over incandescent copper (to remove any possible oxygen), and through 3 tubes, each a metre long and 2.5 cm. in diameter, filled respectively with calcium chloride, powdered potassium hydroxide, and phosphoric oxide, to dry it. It was then absorbed in metallic palladium (p. 279), whence it was regained by heating when required for the experiment.

Pure oxygen was obtained by heating pure potassium chlorate. Exhaustive tests proved that it did not contain more than infinitesimal traces of impurities (e.g. chlorine, carbon dioxide, nitrogen); it was dried by passage through a long tube containing phosphoric oxide. Known weights of both gases were then stored in large

weighed globes, from which they could be introduced into the apparatus.

This was evacuated by means of an efficient pump and weighed. The lower portion was immersed in a freezing-mixture, and the gases were then allowed to flow in, as shown in the figure, the oxygen being in slight excess. On passing a spark, the hydrogen

ignited and continued to burn in the oxygen, and the rate of inflow of the gases was so regulated that the formation of water condensed in the lower part of the apparatus was continuous. The combination of forty-two litres of hydrogen with twenty-one litres of oxygen took about $1\frac{1}{2}$ hours. When sufficient water had collected, it was frozen in the lower tube, and the residual mixture of hydrogen and oxygen in the apparatus was pumped off, weighed, and analysed; the phosphoric oxide in the side arms prevented loss of water. The weights of hydrogen and oxygen remaining in the globes were also determined, so that the weights of the gases used could now be calculated. The weight of water formed served as a check on these figures.

Morley's results were as follows:

<i>Hydrogen used</i>	<i>Oxygen used</i>	<i>Ratio, O : H</i>
3.2645	25.9176	7.939
3.2559	25.8531	7.941
3.8193	30.3210	7.939
3.8450	30.5294	7.940
3.8382	30.4700	7.939
3.8523	30.5818	7.939
3.8297	30.4013	7.939
3.8286	30.3966	7.939
3.8225	30.3497	7.940
3.8220	30.3479	7.941
3.7637	29.8865	7.941
3.8211	30.3429	7.941

The mean value was:

$$\text{Hydrogen : oxygen} = 1 : 7.9395.$$

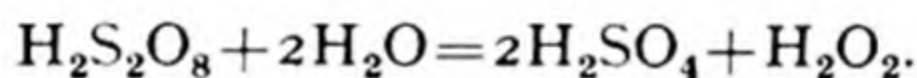
Hence the atomic weight of oxygen, taking $H=1.000$, is 15.878; or the atomic weight of hydrogen, taking $O=16.0000$, is 1.0076. Since Morley used some excess of oxygen, it was possible that the synthesized water contained traces of hydrogen peroxide, for which no tests seem to have been applied. In consequence of this remaining uncertainty, Burt and Edgar repeated Morley's work (1911), using a somewhat different method, allowing an excess of *hydrogen* to be always present. Their results, however, confirmed Morley's figures.

HYDROGEN PEROXIDE, H_2O_2

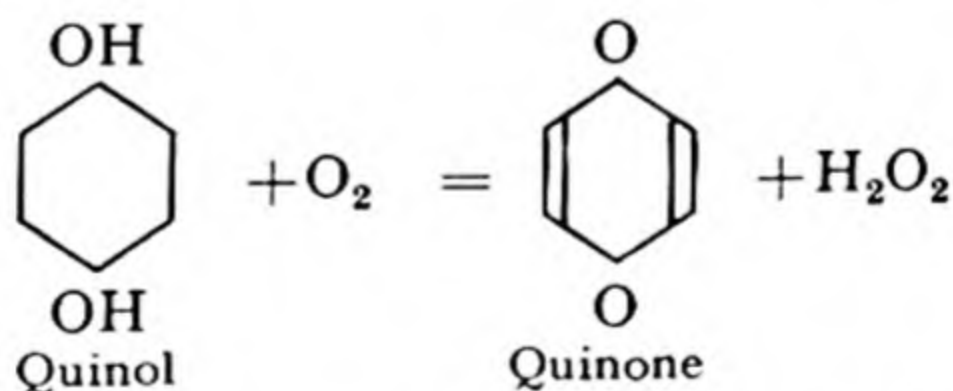
History. Hydrogen peroxide was discovered in 1818 by THENARD, who obtained it by the action of dilute acids upon barium peroxide, BaO_2 (p. 349). He called it *oxygenated water*, and recognized that, relatively to the same quantity of hydrogen, it contains twice as much oxygen as water does. Owing to the readiness with which it decomposes, hydrogen peroxide is difficult to prepare in the pure state, but in 1894 WOLFFENSTEIN succeeded in obtaining the anhydrous substance.

Occurrence. Minute traces of hydrogen peroxide have been reported to exist in snow, in water exposed to brilliant sunshine, in dew, in air, and in certain plants; but since it is by no means easy to distinguish traces of hydrogen peroxide from traces of other oxidizing agents, it would be desirable to have confirmation of these observations.

Preparation. Hydrogen peroxide has important industrial applications and is therefore manufactured on a large scale. Former methods were based upon (a) the treatment with acid (usually phosphoric acid) of barium peroxide, BaO_2 , obtained by heating the monoxide in air, (b) the anodic oxidation of sulphuric acid to peroxydisulphuric acid, $\text{H}_2\text{S}_2\text{O}_8$ (p. 535), followed by the hydrolysis of this acid:



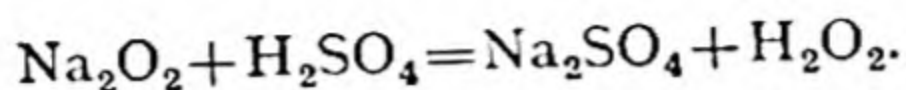
In the process used at the present time the peroxide is synthesized essentially from its elements. A stream of air is passed through solutions of certain quinols in organic solvents, when the following type of oxidation occurs:



Here the reaction has been exemplified with the simplest quinol, *p*-dihydroxybenzene, but actually in the present-day manufacture of hydrogen peroxide more complex quinols (e.g. anthraquinol) are used, which afford a better yield. The peroxide is extracted into water from the organic solvent, and the aqueous solution concentrated by fractionation at low pressure to about 85–90 per cent peroxide ('High Test Peroxide'). The quinone is reduced back to quinol by hydrogen acting with a palladium catalyst.

In the laboratory, a solution of hydrogen peroxide is conveniently prepared by adding sodium peroxide, a little at a

time, to dilute (1 in 5) sulphuric acid surrounded by a freezing-mixture. The addition is continued until the acid is very nearly neutralized:



Most of the sodium sulphate separates out as crystals of the decahydrate, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, and the remaining liquid is poured off.

A solution of hydrogen peroxide may be concentrated to about 50 per cent by evaporation in an open dish on a water-bath at 75° – 100° , but since the peroxide is fairly volatile and liable to decompose, further concentration must be effected by distillation under reduced pressure. In this way, practically anhydrous hydrogen peroxide can be obtained—though, even when special precautions are taken, there is always grave risk of explosion.

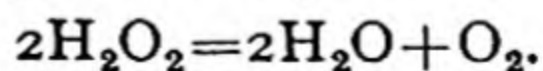
On freezing a dilute solution of hydrogen peroxide, ice separates out and may be removed. The remaining liquid is therefore more concentrated, and by a repetition of the process nearly pure hydrogen peroxide may be prepared.

Properties. Hydrogen peroxide is a viscous liquid, resembling water in being colourless in small quantity but blue when observed in thick layers. It has a specific gravity of 1.463 at 0° , freezes at -1° to a white crystalline solid, and boils at 84° under 68 mm. pressure. It mixes with water in all proportions and is soluble in ether, aniline, alcohol, and other organic liquids.

Aqueous solutions of hydrogen peroxide have a feeble acid reaction and slowly decompose into water and oxygen, the change being accelerated by heat and by alkalis but hindered by acids. Commercial solutions of the peroxide are therefore slightly acidified with sulphuric acid, phosphoric acid, or barbituric acid. Glycerol also retards the decomposition, while dust, manganese dioxide, platinum black, and particularly colloidal platinum, act as positive catalysts and cause rapid evolution of oxygen. Thus, if a pinch of manganese dioxide is added to a solution of hydrogen peroxide, vigorous effervescence takes place in the cold.

Copper salts have a very pronounced catalytic effect upon the decomposition of hydrogen peroxide solutions. A solution containing 30 gm. H_2O_2 per litre and 10 parts per million of copper was found to lose 57.4 per cent of its peroxide after refluxing for 1 hour, and 96.3 per cent after 2 hours.

The concentration of hydrogen peroxide solutions is often expressed in terms of the volume of oxygen evolved when the peroxide is decomposed according to the equation:

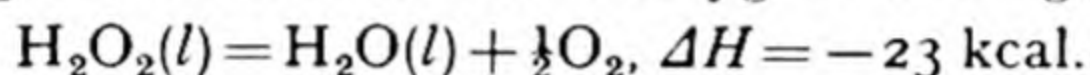


A '10-volume' solution, for instance, is such that 1 c.c. of it will

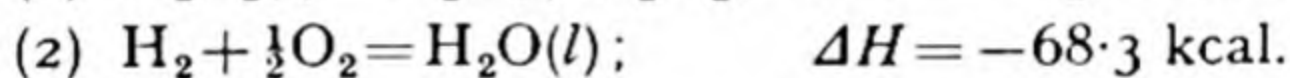
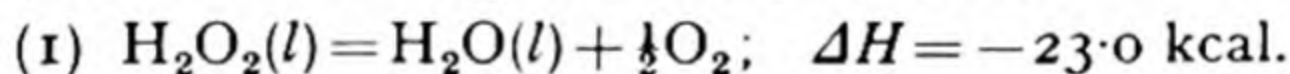
yield 10 c.c. of oxygen; a '20-volume' solution will give 20 times its own volume of oxygen; and so on. Commercial solutions are made up in 10-, 12-, 20-, 100-, and 130-volume strengths. Their concentrations in grams of hydrogen peroxide per litre may easily be calculated from the equation given above. $2(2+32)$ gm. H_2O_2 yield 22.4 litres of oxygen at N.T.P.; hence 1 gm. of H_2O_2 yields 329 c.c. Now 1 litre of '10-volume' hydrogen peroxide gives 10,000 c.c. of oxygen and therefore contains $\frac{10,000}{329}$ gm., i.e. 30.4 gm., H_2O_2 . Similarly '100-volume' and '130-volume' solutions contain about 300 gm. and 400 gm., respectively, of hydrogen peroxide per litre.

Hydrogen peroxide has also been put on the market, under the name of 'hyperol,' as a compound of urea, $\text{CO}(\text{NH}_2)_2$, with hydrogen peroxide of crystallization, $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{O}_2$. On dissolving the compound in water the peroxide is set free.

The instability of hydrogen peroxide is associated with the fact that its decomposition into water and oxygen is strongly exothermic:



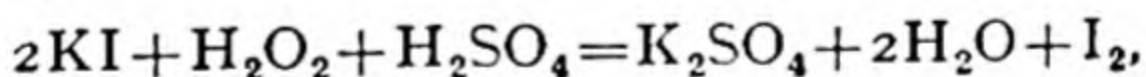
It should not, however, be imagined that hydrogen peroxide is therefore an endothermic compound; on the contrary, it is decidedly exothermic, as the following calculation shows:



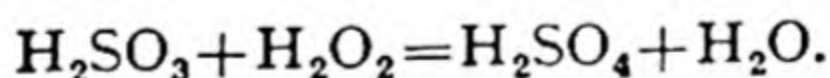
Subtract (1) from (2):



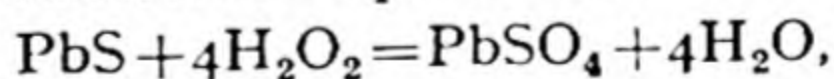
The most conspicuous property of hydrogen peroxide is its dual capacity for oxidation and reduction; thus it will liberate iodine from acidified potassium iodide solution:



and converts sulphurous acid into sulphuric acid:

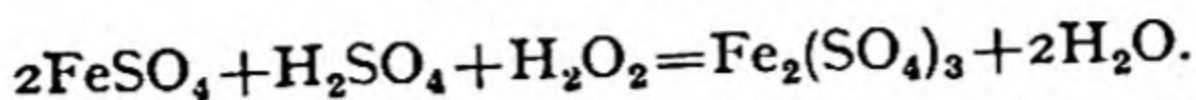


It will also oxidize black lead sulphide into white lead sulphate:

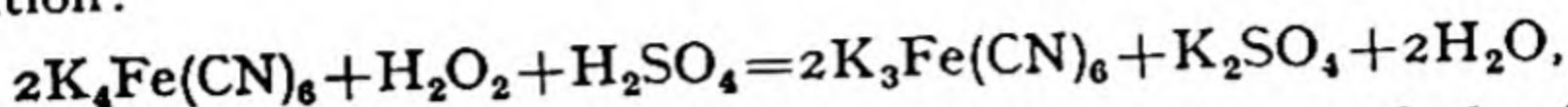


a reaction which has been put to practical use in restoring oil-paintings. The basis of the pigments in oil paints is white lead (p. 422), and this is slowly converted into lead sulphide by the action of the traces of hydrogen sulphide which occur in town air.

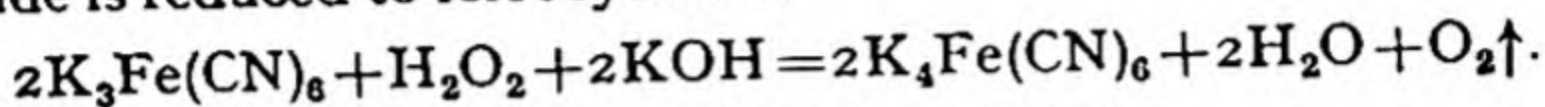
In acid solution, hydrogen peroxide will oxidize ferrous salts to ferric salts:



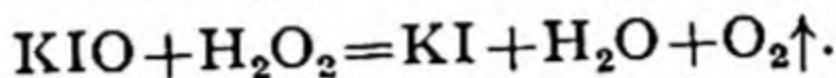
Hydrogen peroxide also acts as a *reducing agent*. Thus, while it oxidizes potassium ferrocyanide to potassium ferricyanide in acid solution:



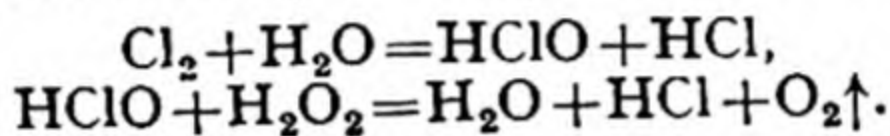
the reverse change takes place in alkaline solution, and the ferricyanide is reduced to ferrocyanide:



It will also reduce alkaline hypoiodites to iodides:

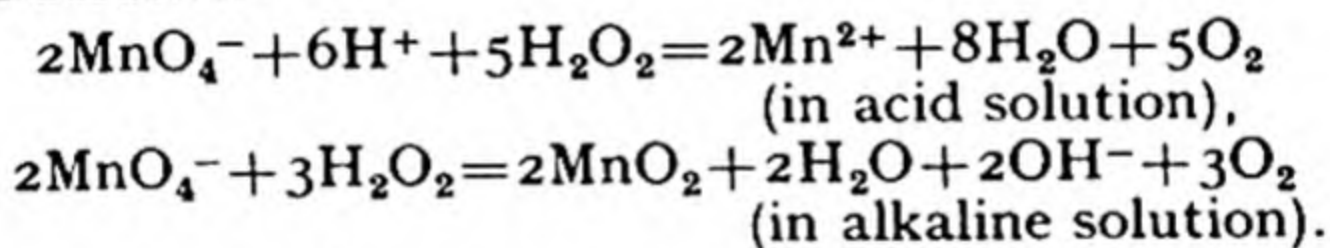


Chlorine water is reduced by it to hydrochloric acid:

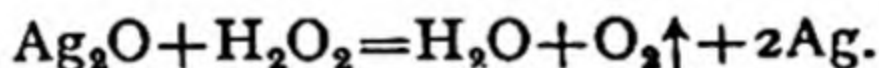


It is upon this reaction that the use of hydrogen peroxide as an antichlor (p. 343) depends.

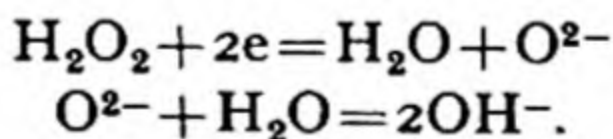
Permanganate is reduced by hydrogen peroxide both in acid and in alkaline solution:



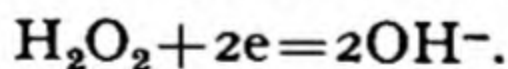
Silver and gold oxides are reduced to the metals by hydrogen peroxide, e.g.:



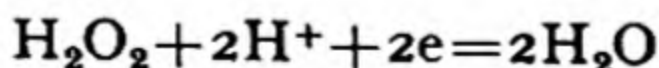
As an oxidizing agent hydrogen peroxide acts as though it were 'oxidized water':



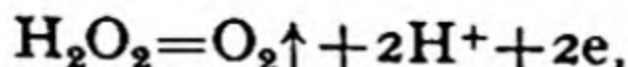
In *alkaline* solution its action is therefore simply:



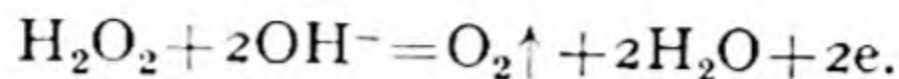
In *acid* solution hydroxyl ion combines with hydrogen ion, and the oxidizing action becomes:



In its reducing actions the peroxide acts as though it were 'reduced oxygen'. In *acid* solution

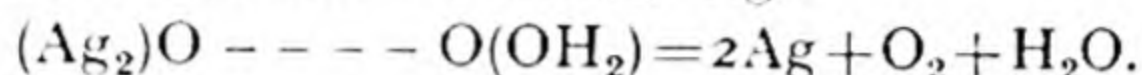


and in *alkaline* solution, in which hydrogen ion combines with hydroxyl ion:

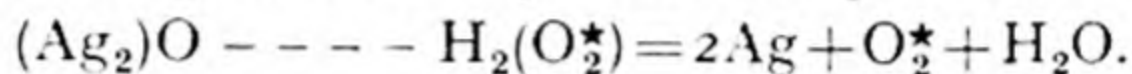


Thus hydrogen peroxide can act in its dual capacity both in acid and alkaline solution, in appropriate conditions. The quantitative treatment in Chapter XVIII, shows that it exerts its strongest *oxidizing* power in *acid* solution, and its strongest *reducing* power in *alkaline* solution.

Isotopic Tracers. Formerly the reducing action of hydrogen was ascribed to a 'mutual reduction,' e.g.:

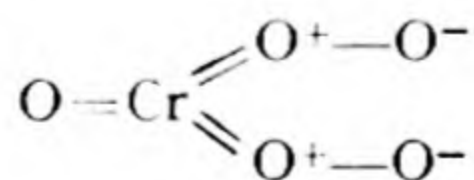


The scheme presented in the preceding section requires, however, that the molecular oxygen liberated in all reductions by hydrogen peroxide should originate wholly from the peroxide:



As long as oxygen atoms were thought to be indistinguishable no decision in favour of one or other of these alternatives was possible. We now know that all natural oxygen and its compounds contain 0.2 per cent of the isotope ^{18}O , which can be concentrated in water by fractional distillation, and released by electrolysis. By burning sodium in the enriched oxygen so obtained and then treating the resulting peroxide with acid, hydrogen peroxide enriched in ^{18}O is produced. The content of ^{18}O in gaseous oxygen is easily determined by accurate density measurements, and by that means it was found that the oxygen released during reductions by enriched peroxide has the same content of ^{18}O as the original peroxide, and is not 'diluted' with ^{16}O from the compound reduced. Since the discovery of isotopes many such outstanding problems have been solved by similar applications of 'isotopic tracers.'

Tests. (i) If dilute sulphuric acid and dilute potassium dichromate solution are added to a solution containing hydrogen peroxide, a blue colour is produced which can be made more marked by shaking the liquid with a little ether; the blue colouring matter, 'perchromic acid,' is extracted by the ether, and the ethereal layer rises to the surface. 'Perchromic acid' is an unstable substance with the probable structure:



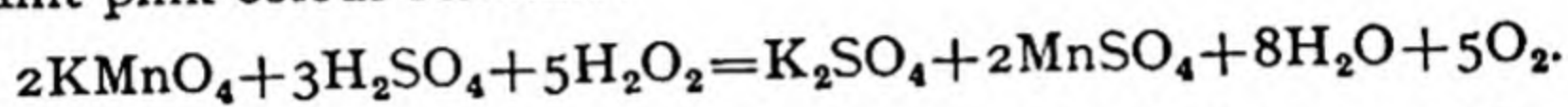
The substance was formerly assigned the formula HCrO_5 and was regarded as an acid.

(ii) A solution of titanium dioxide, TiO_2 , in concentrated sulphuric acid gives an orange-red or yellow colour with hydrogen peroxide, owing to the formation of titanium hydroperoxide or 'pertitanic acid' $(\text{OH})_3\text{Ti}-\text{O}-\text{OH}$.

(iii) Tincture of guaiacum (a resin obtained from the trunk of the tropical American tree *Guaiacum officinale*), mixed with a few drops of blood, gives a blue coloration with hydrogen peroxide. Conversely this colour reaction may be used as a test for blood.

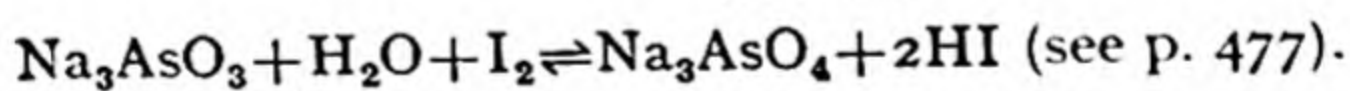
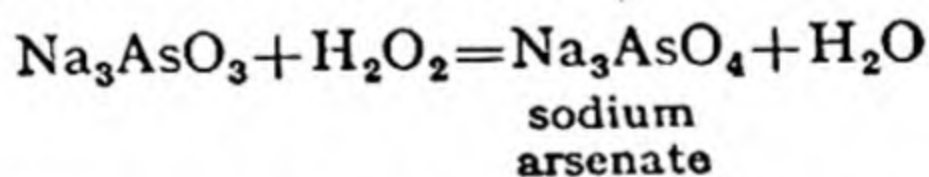
(iv) The liberation of iodine from acidified potassium iodide solution is effected by hydrogen peroxide in common with many other oxidizing agents. If the amount of iodine set free is small, its presence should be confirmed by the addition of starch (p. 565).

Estimation. Hydrogen peroxide may be estimated by titration with standard potassium permanganate in the presence of dilute sulphuric acid, addition of the permanganate being continued until a faint pink colour remains:

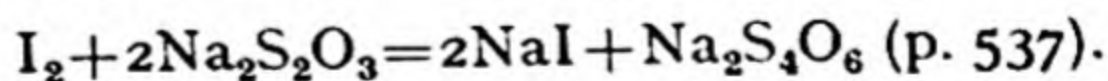
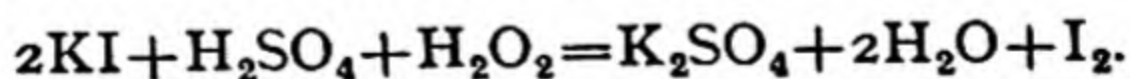


316 grams of KMnO_4 oxidize 170 grams of hydrogen peroxide, and since decinormal permanganate contains 3.16 gm. KMnO_4 per litre, 1 litre N/10 KMnO_4 oxidizes 1.7 gm. of hydrogen peroxide.

If the hydrogen peroxide solution contains barbituric acid, glycerol, or other organic preservative, the result by this method will be too high, since the organic matter will itself be oxidized by the permanganate. An alternative method is to add a known volume of the peroxide solution to a known volume, in excess, of standard sodium arsenite solution, back-titrating the excess of arsenite with standard iodine solution:



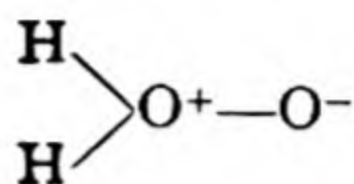
A third method of estimating hydrogen peroxide is to acidify the solution with sulphuric acid, add an excess of potassium iodide, and estimate the liberated iodine with standard sodium thiosulphate:



In estimating very dilute solutions in this way it is advisable to add a few drops of ammonium molybdate solution (made up without addition of nitric acid), which greatly accelerates catalytically the liberation of iodine from potassium iodide in acid solution.

Formula. Since 34 grams of hydrogen peroxide on decomposition yield 18 grams of water and 16 grams of oxygen, its empirical formula must be HO. Cryoscopically the molecular weight is found to be 34. Hence the true formula is H_2O_2 .

X-ray examination of 'hyperol' proves the structure of the hydrogen peroxide molecule to be $\text{HO}-\text{OH}$. This does not preclude the possibility of the existence in *solution* of the tautomeric form



Uses. Hydrogen peroxide is an efficient antiseptic, and since the products of its decomposition—water and oxygen—are both harmless it is widely used in medicine, dentistry, etc. Its taste is astringent.

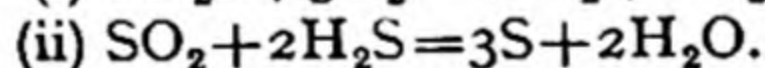
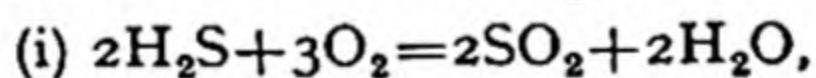
The chief use of hydrogen peroxide, however, is in bleaching, which it effects by oxidation. It was first used in France, in 1878, for the bleaching of silk, but is now employed for bleaching wool, cotton, and artificial silk as well. The cleaned fabrics or articles are heated for some time in a bath of dilute peroxide made alkaline by the addition of sodium silicate. Where an enhanced white is required, sodium pyrophosphate and sodium oxalate or oxalic acid are added to the bleaching bath. Hydrogen peroxide contains a higher proportion (47 per cent) of available oxygen than any other known compound which is liquid at ordinary temperature. It is consequently used as a component of rocket fuels in conjunction with such liquid combustible compounds as hydrazine, N_2H_4 , methanol, CH_4O , or the higher boranes, e.g. pentaborane, B_5H_9 .

SULPHUR, S

Atomic number: 16. Atomic weight: 32.066. Specific gravity: 2.0. Melting-point: 115°. Boiling-point: 445°.

History. Sulphur or brimstone (i.e. 'burn-stone') has been known from the earliest times, for deposits of the free element are found in many parts of the world. HOMER in the *Odyssey* describes it as 'the healer of ills,' a reference to the germicidal powers of the sulphur dioxide obtained by burning it. PLINY recommends it for removing lichens from the face and as a remedy for the stings of scorpions, while BARTHOLOMEW THE ENGLISHMAN (thirteenth century) says that there are four kinds of sulphur, one of which is 'sometimes great and boisterous and full of drausts [dross].' SIR THOMAS BROWNE (1605-82) describes brimstone as a 'mineral body of fat and inflammable parts, and this is used either crude, and called *sulphur vive*, and is of a sadder colour, or after depuration [purification], such as we have in magdaleons or rolls, of a lighter colour.' The alchemists regarded metals as compounds of sulphur with mercury, while during the eighteenth century sulphur was considered to be a compound of sulphuric acid and phlogiston. That, in fact, sulphur is an element was first realized by LAVOISIER (1743-94).

Occurrence. Large quantities of free sulphur occur in Sicily, New Zealand, Japan, and other volcanic districts, but most of the sulphur of commerce is obtained from the vast subterranean beds in Louisiana and Texas, U.S.A. When associated with volcanoes, the sulphur has probably been formed by the incomplete combustion of the hydrogen sulphide in the volcanic gases:



In other cases the deposits may have been produced by bacterial action upon sulphates or as the effect of heat upon a mixture of sulphates and bitumen (natural pitch).

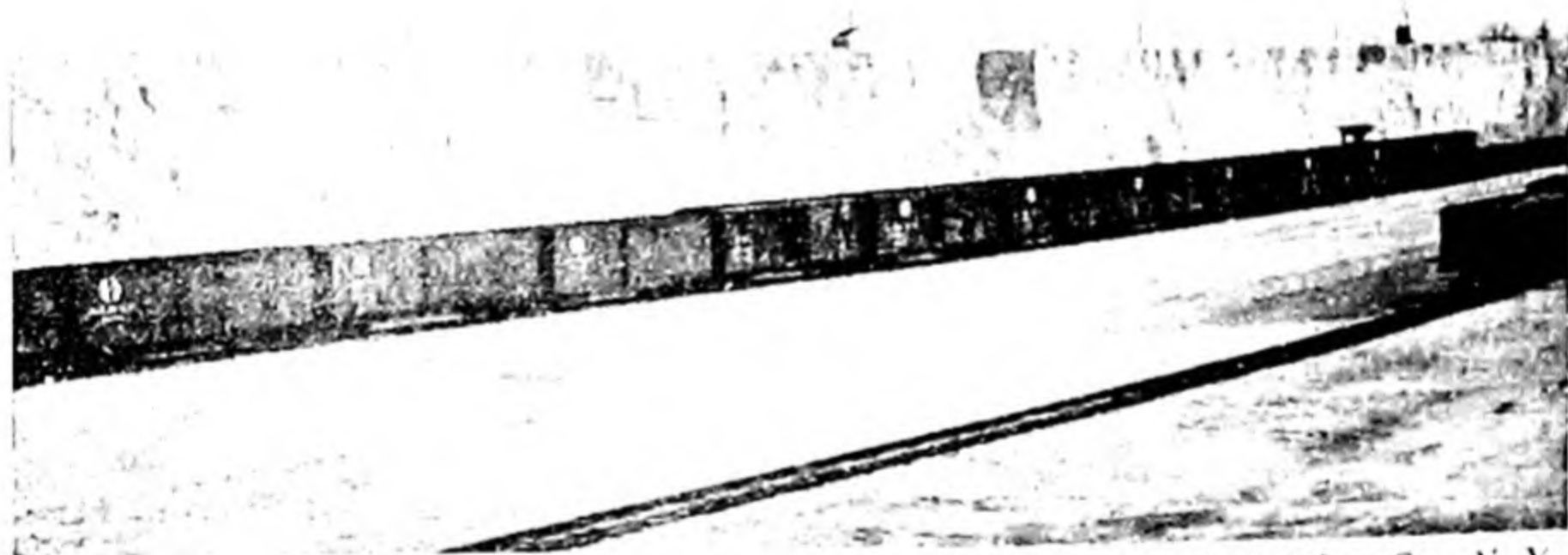
Among the chief naturally occurring compounds of sulphur are the *sulphides* of various metals, e.g. *iron pyrites*, FeS_2 ; *copper pyrites*, $CuFeS_2$; *galena*, or *lead sulphide*, PbS ; *zinc blende*, or *zinc sulphide*, ZnS ; and *cinnabar*, or *mercuric sulphide*, HgS . With the exception of iron pyrites (from which sulphur dioxide is manufactured), all these sulphides form the principal ores of the metals they contain.

Certain sulphates also occur naturally, e.g. *calcium sulphate*, $CaSO_4$, which is found as *gypsum* and *alabaster*, $CaSO_4 \cdot 2H_2O$, as well as in the anhydrous state as the mineral *anhydrite*; *magnesium*

sulphate, or *Epsom salt*, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$; and *barium sulphate*, or *heavy spar*, BaSO_4 .

Sulphur is a constituent of living matter, the proteins of peas, beans, and lentils containing as much as 2 per cent of it. Animal proteins also contain sulphur, while the characteristic smell of mustard, garlic, and onions is due to sulphur compounds.

Extraction. Nearly 80 per cent of the total sulphur output comes from Louisiana and Texas. The deposit forms a large bed—estimated to contain over 40,000,000 tons—beneath 600 feet



Texas Gulf Sulphur Co., N. Y.

FIG. 93. BLOCK OF SULPHUR IN TEXAS

of rock, quicksand, and clay. Its existence had been known for nearly forty years before its successful exploitation became possible, but about 1904 FRASCH solved an exasperating problem by a method both simple and elegant.

Frasch's process consists in driving four co-axial steel pipes, the largest being about 1 foot in diameter, down to the layer of sulphur. In the diagram (Fig. 94), the two outer pipes have been represented as one (Pipe I), for greater simplicity. Down these two pipes, water superheated to about 180° is forced under considerable pressure. The heat of the water melts the sulphur near the bottom of the pipe, so that a pool of the liquid element collects there. Through Pipe III a blast of hot compressed air is now blown, when a froth of liquid sulphur, steam, and air is forced up through Pipe II. The liquid

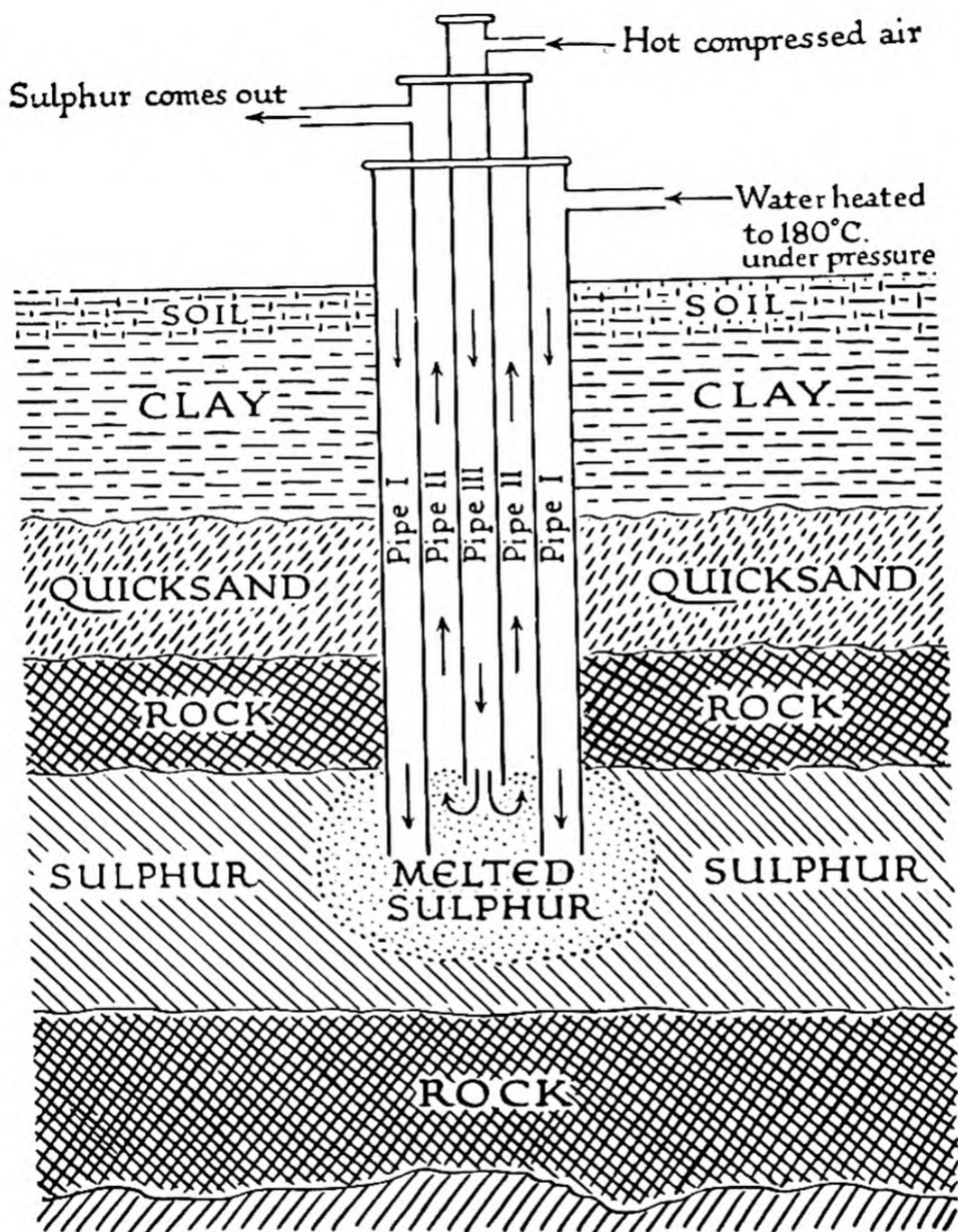


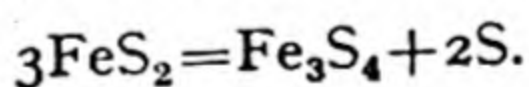
FIG. 94. FRASCH'S PROCESS

sulphur is run into enormous wooden bins, where it soon solidifies. When a bin is full it may contain a solid block of sulphur weighing as much as 150,000 tons—probably the largest single piece of any element ever produced. The sulphur is practically pure (about 99.5 per cent), and a single 'sulphur well' may produce 400–500 tons daily. The sulphur in the bin is blasted by explosives and loaded into trucks for transport.

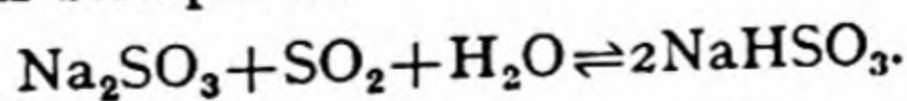
In Sicily, which was formerly the chief sulphur-producing country but has now been badly hit by the American competition, sulphur occurs mixed with limestone, gypsum, clay, and other impurities. The method of extracting it has been in use since the Dark Ages, and although somewhat improved in recent times it is still very wasteful. The ore is first quarried and carried to the surface, where it is stacked into mounds called *calcaroni*. Each mound is covered with a layer of ash, and the sulphur at the bottom is then ignited. The heat produced by the combustion of part of the sulphur is sufficient to melt the rest, which runs out at the bottom of the mound and is collected in wet wooden troughs. By using special furnaces, e.g. the Gill and San Filippo furnaces, the waste of sulphur is lessened. The Sicilians have, indeed, become so highly skilled in the work that only about one-third of the sulphur is lost by combustion, and since fuel is exorbitantly dear in Sicily it is actually less expensive to use a portion of the sulphur for this purpose than to heat the *calcaroni* with imported coal. In the Romagna (i.e. the provinces of Bologna, Ferrara, Ravenna, and Forlì, in Italy), where sulphur is also mined, the heating is effected by means of superheated steam, and the yield can then be increased to nearly 90 per cent.

The Sicilian sulphur is only about 96 per cent pure, but for many purposes may be used in the crude state. It can be purified by distillation.

Smaller quantities of sulphur are obtained by strongly heating iron pyrites in fireclay retorts, when about one-third of the original sulphur is set free and distils over:

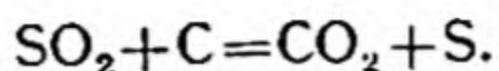


Of recent years, much sulphur has been recovered from the SO_2 contained in the gases formed during the roasting of sulphide ores of zinc, copper, lead, and nickel. The dilute gases are passed through a solution containing sodium sulphite, which removes the sulphur dioxide as bisulphite:



On heating to 100° , the bisulphite is decomposed into the sulphite, water, and nearly pure sulphur dioxide. This is dried by cooling,

and then passed over coke heated to $1,100^{\circ}$, when the following reaction occurs:



The change is practically complete, and is exothermic (-13.2 kcal.) at the working temperature; once started, therefore, it proceeds without the application of external heat. The formation of undesirable by-products, e.g. carbon monoxide, CO , and carbonyl sulphide, COS , is avoided by the use of catalysts.

One important feature of this process is that it provides a means of obtaining sulphur from anhydrite, CaSO_4 , large deposits of which occur in this country. When anhydrite is heated with clay and coke, cement clinker is formed and sulphur dioxide is evolved. The sulphur dioxide was formerly allowed to go to waste (except for such as was required in making sulphuric acid), but the sulphur in it can now be recovered.

Chemically pure sulphur. It is by no means a simple task to obtain chemically pure sulphur, and the difficulty is increased by the fact that, at temperatures in the region of 300° , sulphur slowly attacks glass, reducing the silicates in it to silicon. According to AYNLEY and ROBINSON, the following method of purification is satisfactory. The crude element is refluxed in a Pyrex flask under dry carbon dioxide for several days. After solidification, the coarsely crushed sulphur is distilled in carbon dioxide, the first and last fractions of the distillate being rejected. The middle fraction is then redistilled five times in a vacuum.

Properties. Sulphur exists in more allotropic forms than any other element. Its chief solid allotropes are:

- (i) α -sulphur, rhombic sulphur, or octahedral sulphur.
- (ii) β -sulphur, monoclinic, or prismatic sulphur.
- (iii) γ -sulphur, amorphous sulphur.

α -Sulphur is the main constituent in ordinary roll sulphur; it consists of octatomic molecules, S_8 (see Fig. 95). The 8 atoms are arranged in two layers of 4. α -Sulphur separates in pure condition from solutions of sulphur in carbon disulphide. If heated quickly to 112.8° , it melts; but if heated at just above 96° it gradually changes into β -sulphur. This, like α -sulphur, is composed of S_8 molecules but the crystal-packing of the molecules differs in the two allotropes. Below 96° , β -sulphur slowly reverts to α -sulphur (specific gravity 2.06). At 96° , neither form shows any tendency to pass into the other; this is therefore the *transition-temperature* (cf. p. 169). *β -Sulphur* can be prepared by melting α -sulphur and allowing the liquid to crystallize; or by the evaporation at 100° of a solution of sulphur in acetylene tetrachloride, $\text{C}_2\text{H}_2\text{Cl}_4$ (B.P. 146°). Its

specific gravity is 1.96. On heating, it melts at 119.3° . Both α - and β -sulphur are soluble in carbon disulphide.

When sulphur is melted as carefully as possible, it forms a clear, honey-coloured, mobile liquid. This consists almost entirely of melted S_8 , but contains some 4 per cent of another allotrope, S_{μ} , and a little S_{π} —which has tetratomic molecules, S_4 . On raising the temperature, the principal changes—the deepening of colour and the great increase in viscosity—are due to the formation of chain polymers, of large molecular weight, by the opening of the S_8 rings (Fig. 95) and the reunion of the short chains so formed into much larger units. As the boiling-point (444.6°) is approached the

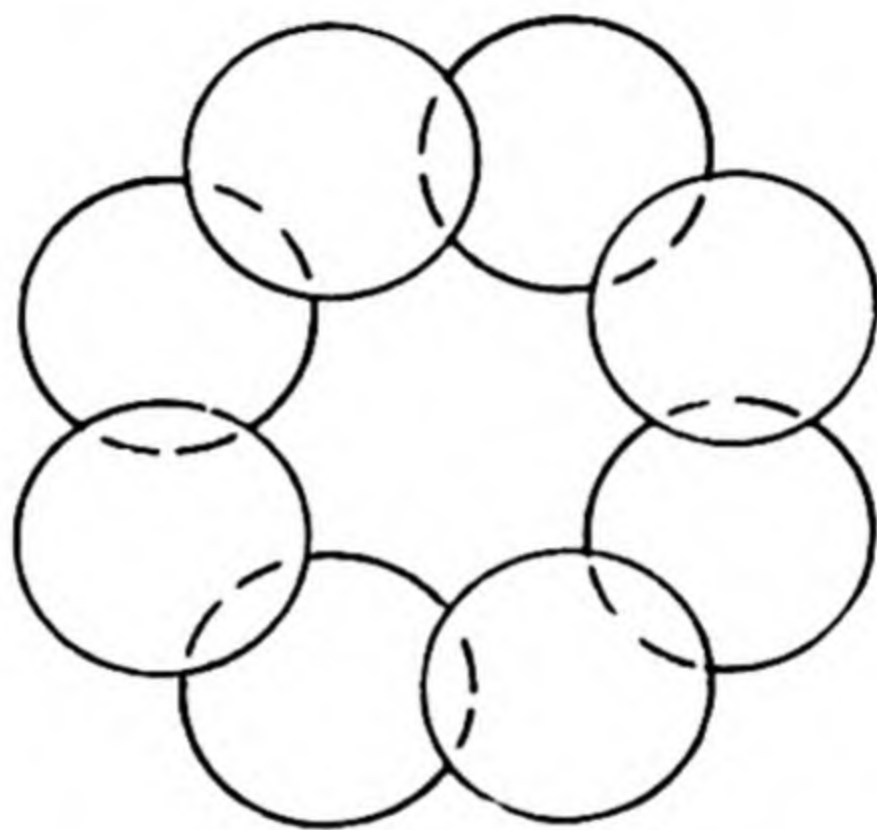


FIG. 95. MOLECULAR STRUCTURE OF S_8

liquid becomes mobile again (though it remains dark), and finally boils to give a dark red vapour. S_{μ} is the liquid form of the amorphous solid allotrope S_{γ} .

On rapidly cooling the liquid in its most viscous state, i.e. with the polymers of greatest molecular weight, the sulphur solidifies in the polymerized form, and the solid has, in common with rubber and other 'elastomers,' the peculiar elastic properties associated with the existence, under certain conditions, of long many-membered chains. On standing at room temperature, re-formation of the cyclic S_8 molecules gradually proceeds, and α -sulphur is ultimately recovered. Almost all forms of solid sulphur not prepared by recrystallization from a solvent appear to contain varying amounts of an allotrope, γ -sulphur, which is insoluble in carbon disulphide. Very little is known about this allotrope, except that it appears from its insolubility to be a form of high molecular weight.

It will be convenient to summarize these facts:

- Liquid sulphur:* at melting-point, molten S_8 , with cyclic molecules: at about 200° to boiling-point, mainly highly polymerized to long chain molecules.
- Plastic sulphur:* 'Elastomer' of polymerized chain molecules: unstable and reverts to α -sulphur.
- α -sulphur: molecules of S_8 packed to give a rhombic crystal.
- β -sulphur: molecules of S_8 packed to give a monoclinic crystal.
- γ -sulphur: stable polymerized form (?): insoluble in carbon disulphide.

Colloidal sulphur is often found in reactions in which the element is liberated in solutions, e.g. in qualitative analysis.

Vapour density determinations show that at low temperatures (200° under reduced pressure), the molecules of gaseous sulphur are S_8 . On heating, the molecular complexity gradually decreases, the vapour density at 900° corresponding to the formula S_2 . At still higher temperatures, further dissociation occurs, and at $2,000^\circ$ sulphur vapour consists of the monatomic molecules S. The reverse changes occur on cooling.

Sulphur is an extremely poor conductor of heat and electricity, and is often used as an insulator. It is insoluble in water, but dissolves in many organic solvents. It is unaffected by air at ordinary temperatures, but takes fire when sufficiently heated, and burns with a blue flame; the chief product of the combustion is sulphur dioxide, SO_2 , but a little sulphur trioxide, SO_3 , is formed simultaneously. Sulphur ignites spontaneously in fluorine, and combines energetically with many metals when the action is started by the application of heat. Mixtures of sulphur with zinc, iron, or copper, for instance, become incandescent when ignited, and the metallic sulphides are formed: ZnS , FeS , Cu_2S , CuS .

Sulphur is resistant to non-oxidizing acids, but is attacked by hot concentrated nitric acid, which converts it into sulphuric acid. It is, however, readily soluble in hot aqueous solutions of alkalis, forming sulphides (p. 521), polysulphides (p. 521), and thiosulphates (p. 536).

Uses. Sulphur is used in the manufacture of sulphuric acid, carbon disulphide, matches, gunpowder, dyes, and calcium bisulphite. It is also employed in vulcanizing rubber, and as a fungicide for vines and hops. Certain cements contain sulphur, while wood impregnated with sulphur is extremely hard and durable. Sulphur ointments are used in the treatment of ringworm and scabies,

and a mixture of sulphur and treacle is an old-fashioned but mild and efficacious laxative (cf. *Nicholas Nickleby*, Chapter VIII).

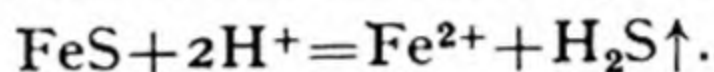
COMPOUNDS OF SULPHUR

Hydrogen sulphide, H_2S , formerly known as sulphuretted hydrogen, occurs naturally in volcanic gases, in the water of certain springs (e.g. Harrogate), and in rotten eggs. It can be synthesized by passing hydrogen through boiling sulphur, but the yield is very poor and the action is reversible:



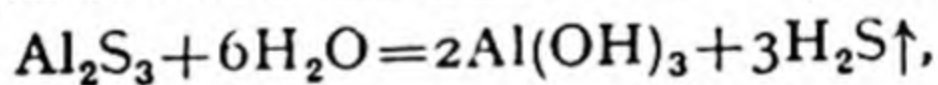
A good yield can be obtained by passing a mixture of hydrogen and sulphur vapour over reduced nickel at 450° .

In the laboratory, hydrogen sulphide is usually prepared by the action of hydrochloric acid on ferrous sulphide:

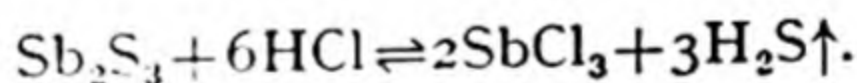


Ferrous sulphide, however, as prepared commercially—viz. by heating iron and sulphur together—always contains free iron and possibly iron carbide and phosphide. The hydrogen sulphide obtained from it is consequently contaminated with hydrogen, phosphine, and hydrocarbons, and since these are difficult to remove, the pure gas is best prepared in other ways, e.g.:

(a) by the action of water on aluminium sulphide:



or (b) by the action of concentrated hydrochloric acid on antimony sulphide:

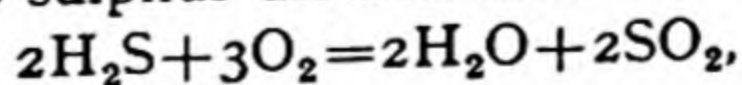


Hydrogen sulphide may be dried with calcium chloride or phosphorus pentoxide, but not with sulphuric acid, which it slowly reduces.

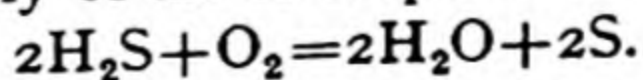
Properties. Hydrogen sulphide is a colourless gas with an unpleasant smell. It is approximately as poisonous as hydrogen cyanide ('prussic acid'), hence no liberties should be taken with it.

On cooling, it condenses to a colourless liquid (B.P. -62°), and this can be frozen to a colourless solid (M.P. -83°).

Hydrogen sulphide is moderately soluble in water, 1 c.c. of water at 0° dissolving 4.7 c.c. of the gas. It is inflammable, burning in a free supply of air to sulphur dioxide and water:

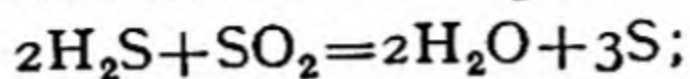


and in a limited supply of air to sulphur and water:

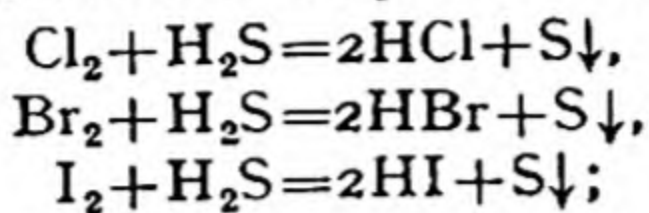


In contact with sodium peroxide, it ignites spontaneously.

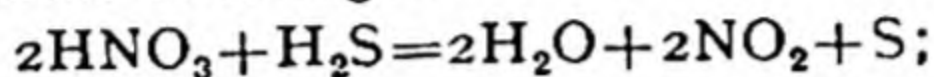
Hydrogen sulphide is a good reducing agent, on account of its instability. Thus it reduces moist sulphur dioxide to sulphur:



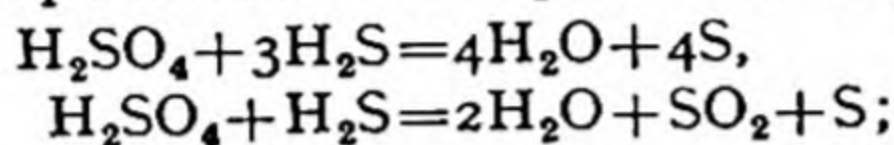
halogens in aqueous solution or suspension to halogen hydracids:



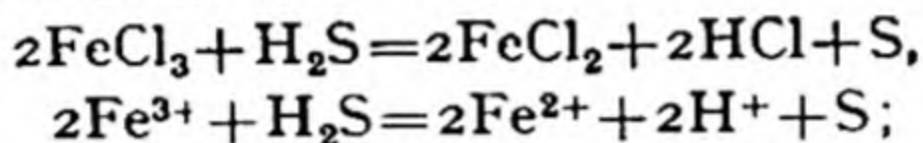
nitric acid to oxides of nitrogen:



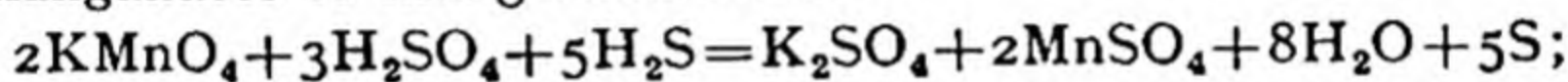
concentrated sulphuric acid to sulphur and sulphur dioxide:



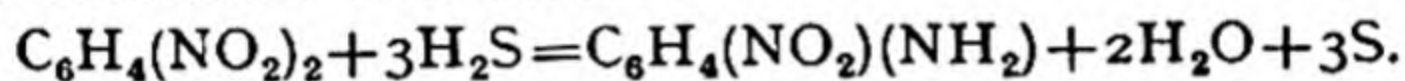
ferric salts to ferrous salts:



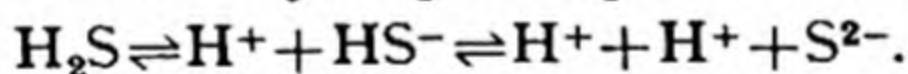
permanganates to manganous salts:



and dinitrobenzene to nitraniline:



An aqueous solution of hydrogen sulphide reacts weakly acid:



The second dissociation occurs to only a very limited degree. Salts of the type K_2S and FeS are called *sulphides*, and those of the type KHS and $\text{Ca}(\text{HS})_2$ are called *hydrosulphides*.

Sulphides and hydrosulphides of the alkali and alkaline-earth metals may be obtained by passing hydrogen sulphide into aqueous solutions of the metallic hydroxides; the sulphides are formed first, but are converted into the hydrosulphide if excess of hydrogen sulphide is used. Both the sulphides and the hydrosulphides of these metals, and of magnesium and ammonium, are soluble in water but are alkaline in solution. Their solutions will dissolve sulphur, to form *polysulphides* of various compositions, e.g. K_2S_2 , K_2S_4 , $(\text{NH}_4)_2\text{S}_5$; these are decomposed by acids, yielding hydrogen sulphide and a precipitate of finely divided sulphur ('milk of sulphur'). Ammonium polysulphide solution is the 'yellow ammonium sulphide' of qualitative analysis.

Insoluble sulphides can often be prepared by precipitation, as in Group II of the analytical tables, but in some cases (e.g. aluminium

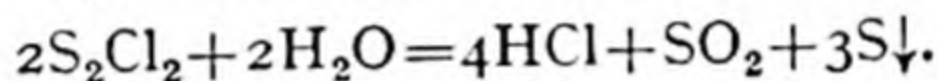
and chromium) the sulphides are completely decomposed by water and the metallic hydroxide is precipitated (cf. p. 383).

Composition. Vapour density is 17, hence $M.W.=34$ and the only possible formula is H_2S . This is confirmed by the fact that, when a metal such as tin is heated in the gas, the volume of hydrogen left is equal to the original volume of hydrogen sulphide.

Hydrogen persulphide, H_2S_2 , is the best known of several hydrogen polysulphides obtained by adding a cold solution of calcium polysulphides to ice-cold hydrochloric acid. It is a pale yellow oil, interesting as the sulphur analogue of hydrogen peroxide.

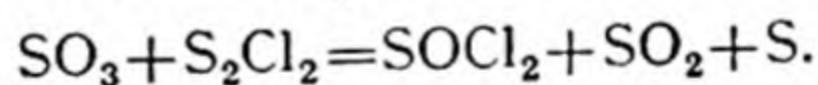
Sulphur halides. No *iodides* of sulphur are known. *Sulphur bromide*, S_2Br_2 , is a red, unstable oil made by the action of bromine on sulphur at 100° .

'*Sulphur monochloride*,' or *disulphur dichloride*, S_2Cl_2 , is an orange-red liquid obtained by passing dry chlorine over melted sulphur in a retort connected to a condenser. A certain amount of the liquid *sulphur dichloride*, SCl_2 , is formed at the same time and remains dissolved in the monochloride. The latter is purified by redistillation, and when pure boils at $138-9^\circ$. Sulphur monochloride, $ClS-SCl$, is hydrolysed by water:



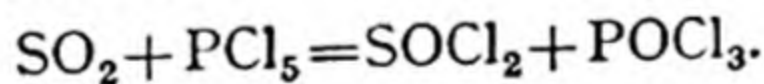
It is used in vulcanizing rubber, and for regenerating acetic anhydride from sodium acetate in the artificial silk industry.

Thionyl chloride, $SOCl_2$, an oxy-halide of sulphur, is prepared industrially by the action of sulphur trioxide on disulphur dichloride:

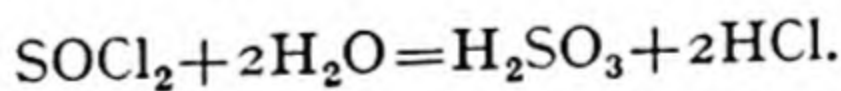


The sulphur liberated is reconverted into S_2Cl_2 by means of chlorine.

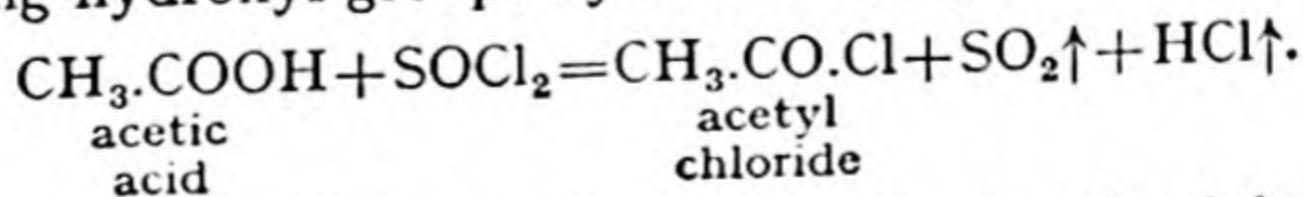
Thionyl chloride is also formed when sulphur dioxide reacts with phosphorus pentachloride:



It is a colourless, fuming liquid, which boils at 79° and is hydrolysed by water:

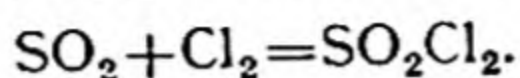


It is, in fact, the acid chloride of sulphurous acid, $SO(OH)_2$. In organic chemistry, thionyl chloride is the most convenient reagent for replacing hydroxyl groups by chlorine, e.g.:

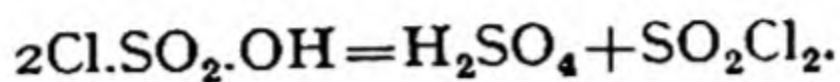


Sulphuryl chloride, SO_2Cl_2 , the acid chloride of sulphuric acid, $SO_2(OH)_2$, is prepared by the direct combination of sulphur

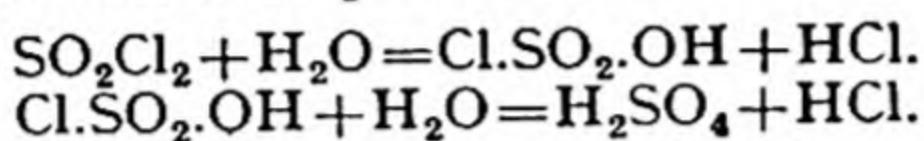
dioxide and chlorine in the presence of sunlight or of certain catalysts, e.g. camphor or activated carbon:



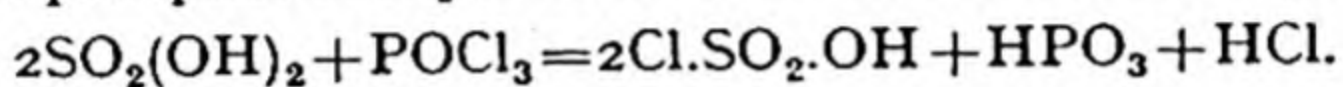
It may also be prepared by heating chlorosulphonic acid (see below) at 180° , either under pressure or with mercuric sulphate as catalyst:



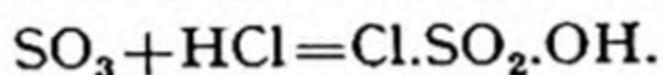
Sulphuryl chloride is a heavy, colourless, oily, fuming liquid (B.P. 69°). It is slowly hydrolysed by water, first to chlorosulphonic acid and then to sulphuric acid:



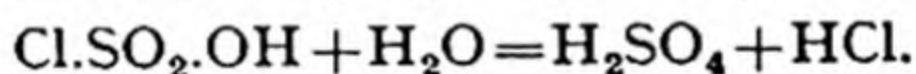
Chlorosulphonic acid, $\text{Cl}.\text{SO}_2.\text{OH}$, is the semi-acid chloride of sulphuric acid. In the laboratory it is prepared by distilling a mixture of phosphorus oxychloride and concentrated sulphuric acid:



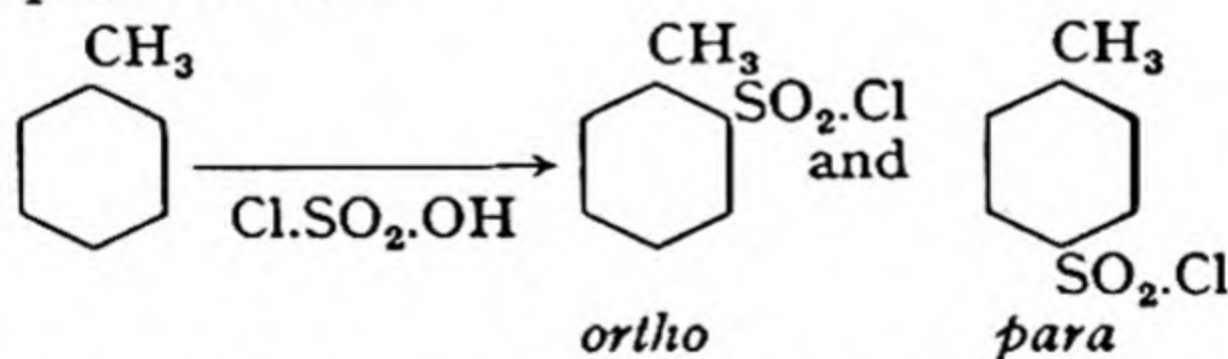
Industrially it is prepared by passing hydrogen chloride into 'oleum':



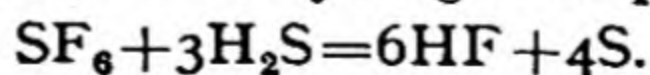
Chlorosulphonic acid is a heavy, colourless, oily, fuming liquid (B.P. 154°) which is violently hydrolysed by water:



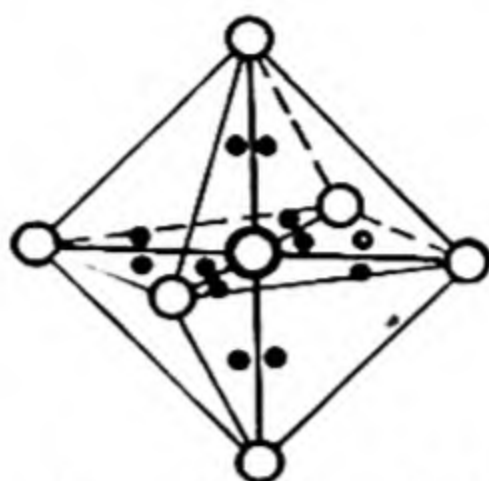
It is used in organic chemistry to sulphonate aromatic compounds; thus toluene is converted by it into a mixture of *ortho*- and *para*-toluene-sulphochlorides:



Sulphur is said to form the *fluorides* S_2F_2 , SF_4 , SF_6 , and S_2F_{10} . Of these *sulphur hexafluoride*, SF_6 , is the best known. It results from the spontaneous combustion of sulphur in fluorine, and is a colourless gas which condenses to a solid, melting at -51° and subliming at -64° . Chemically it is remarkable for its lack of activity; thus it is unaffected by water, by aqueous or fused alkali, and by red-hot copper. It is, however, decomposed by boiling sodium, and reacts with hydrogen sulphide as follows:



The great stability of sulphur hexafluoride is perhaps associated with the fact that both sulphur and fluorine are here exerting their maximum covalencies:

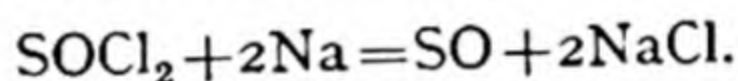


Oxides and oxyacids of sulphur. Sulphur forms the following oxides:

SO	sulphur monoxide	SO ₃	<i>sulphur trioxide</i>
S ₂ O ₃	sulphur sesquioxide	S ₂ O ₇	sulphur heptoxide
SO ₂	<i>sulphur dioxide</i>	SO ₄	sulphur tetroxide.

Of these the most important are italicized. The oxyacids of sulphur corresponding to various oxides are described in the appropriate places.

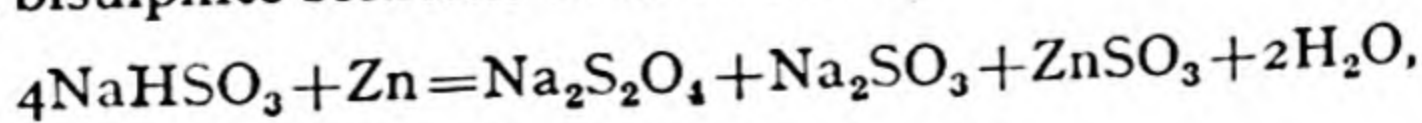
Sulphur monoxide, SO, can be prepared in several ways, e.g. by the action of sodium on thionyl chloride:



It is a colourless gas, unstable at room temperature ($2\text{SO} \rightarrow \text{SO}_2 + \text{S}$), which, when cooled in liquid air, condenses to an orange-red solid. It reacts with chlorine to form thionyl chloride, and with water to give a mixture of hydrogen sulphide, sulphur dioxide, and sulphur. Liquid sulphur monoxide is strongly magnetic, like liquid oxygen. There is no corresponding oxyacid of which it is the anhydride.

Sulphur sesquioxide, S₂O₃, is a bluish-green solid made by the addition of sulphur to melted sulphur trioxide. It is stable up to 15°, but on heating decomposes into sulphur, sulphur monoxide, and sulphur trioxide. From its formula, and that of *dithionous acid*, H₂S₂O₄, one might expect it to be dithionous anhydride, but when it reacts with water it gives a complex mixture of acids among which H₂S₂O₄ is not included. Probably, therefore, H₂S₂O₄ and S₂O₃ have very different types of structure.

Dithionous acid itself is unknown, but various metallic *dithionites*, e.g. Na₂S₂O₄, have been prepared. They are unstable and are powerful reducing agents. The sodium salt, made by reducing sodium bisulphite solution with zinc dust:



is used in refining sugar and in the dye industry. When aqueous sodium bisulphite is reduced by zinc in the presence of formaldehyde, a compound of the formula $\text{Na}(\text{O}_2\text{S}-\text{CH}(\text{OH})_2)$ is formed. This is used commercially under the name of 'rongalite,' and it forms a derivative of the hypothetical sulphonylic acid, H_2SO_2 ; it is a powerful reducing agent.

Sulphur dioxide, SO_2 , the most familiar oxide of sulphur, is prepared commercially by the combustion of sulphur or sulphide minerals (iron pyrites, copper pyrites, galena, zinc blende). It is filtered through coke, dissolved in cold water, re-obtained in a purer form by heating the solution (or by lowering the external pressure), dried with sulphuric acid, and compressed to a liquid at 3 atmospheres. It is marketed as the liquid, in glass siphons, etc.

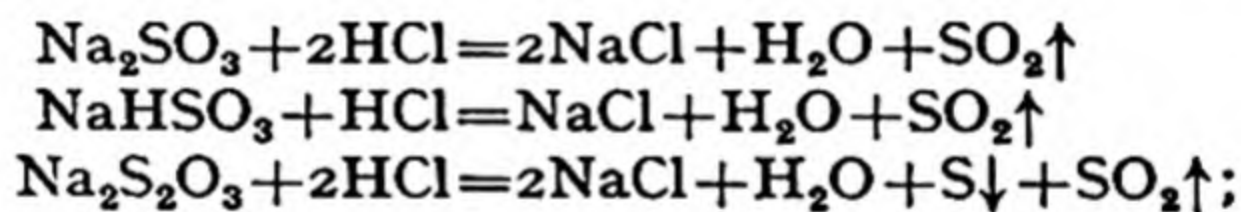
It can be prepared in the laboratory by heating copper turnings with concentrated sulphuric acid. The residue is black in colour and contains cupric sulphate, cuprous sulphide, Cu_2S , and cupric sulphide, CuS . The usual equation:



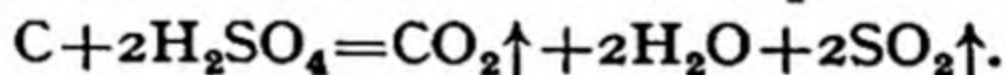
is not even an approximation to the truth, but if mercury is substituted for copper pure sulphur dioxide is obtained and there are no side-reactions.

Sulphur dioxide is also formed when

(a) a sulphite, bisulphite, or thiosulphate is treated with a dilute acid:

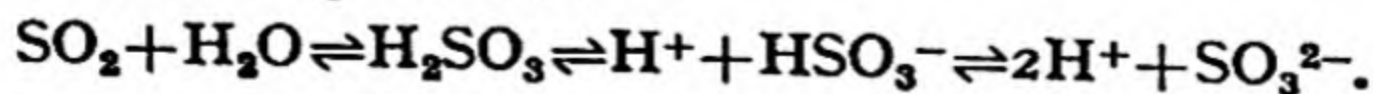


(b) carbon is heated with concentrated sulphuric acid:



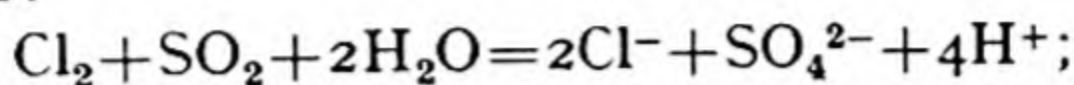
Properties. Sulphur dioxide is a heavy, colourless gas with a pungent smell; it is poisonous, especially to the lower forms of life, and is used as a disinfectant. Since its critical temperature (157°) is far above room temperature, it may be condensed in the laboratory by increase of pressure alone. It also liquefies if passed at atmospheric pressure through a freezing-mixture of ice and salt. The liquid boils at -10° , and is an ionizing solvent, i.e. it dissolves certain electrolytes to give solutions which contain ions of the solute. In this respect it resembles water and liquid ammonia.

Sulphur dioxide is very soluble in water, 80 c.c. of the gas dissolving in 1 c.c. of water at 0° . Partial combination occurs in solution, sulphurous acid being formed:

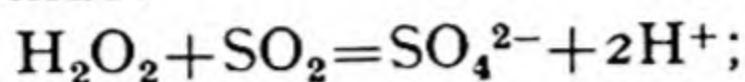


Sulphur dioxide generally acts as a reducing agent, especially in solution. The solution reduces

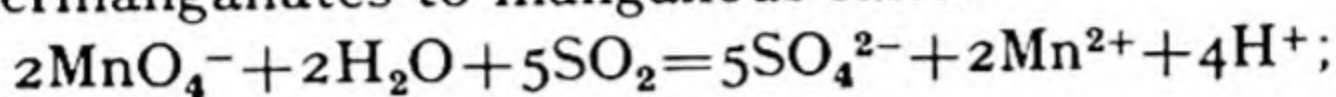
(a) halogens:



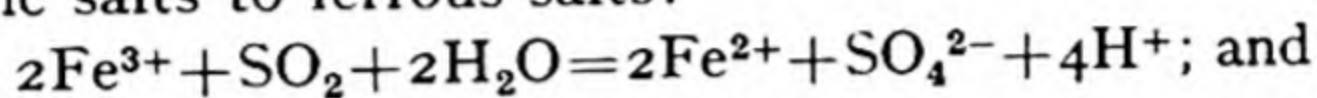
(b) hydrogen peroxide:



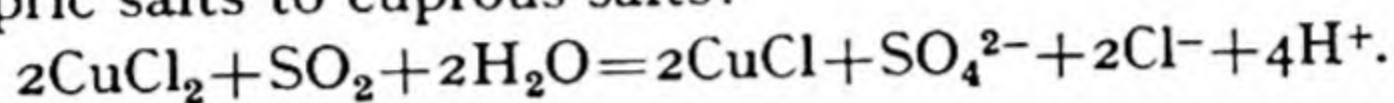
(c) permanganates to manganous salts:



(d) ferric salts to ferrous salts:

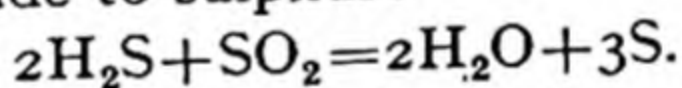


(e) cupric salts to cuprous salts:

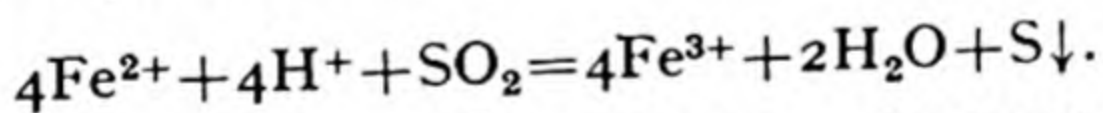


It will reduce many dyes and natural colouring-matters to colourless compounds, and is frequently employed in bleaching fabrics or substances that would be damaged by chlorine or bleaching-powder. Since the reduction does not in general disintegrate the molecules of the colouring-matter, atmospheric oxidation may slowly restore the original colour.

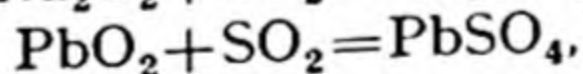
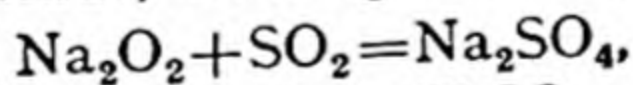
Although sulphur dioxide in solution is typically a reducing agent, it may also behave as an oxidizing agent. For example, it oxidizes moist hydrogen sulphide to sulphur:



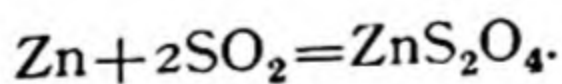
Under certain conditions, e.g. large excess of acid, it will oxidize cuprous, stannous, ferrous, and mercurous salts to the corresponding -ic salts:



Sulphur dioxide will combine with incandescence with sodium peroxide and lead dioxide, forming the sulphates:



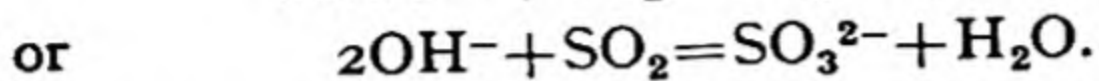
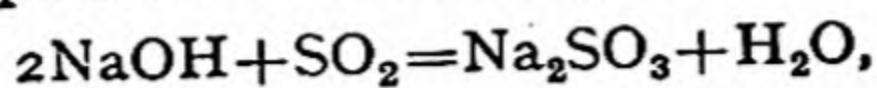
and in aqueous solution will dissolve zinc to form zinc dithionite:



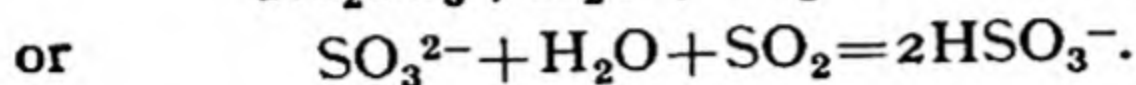
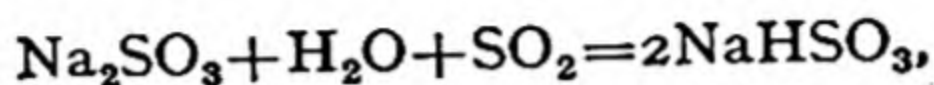
The catalytic oxidation of sulphur dioxide to sulphur trioxide is the basis of the manufacture of sulphuric acid (p. 528).

Sulphurous acid, H_2SO_3 , exists only in aqueous solution, and is so unstable that all attempts to isolate it result in its decomposition into water and sulphur dioxide. It is, however, a fairly strong acid, and gives rise to two series of salts, the *sulphites* and the *bisulphites*.

Sodium sulphite, Na_2SO_3 , is the first product to be formed when sulphur dioxide is passed into sodium hydroxide solution:



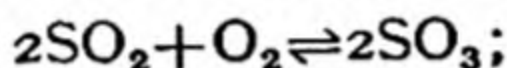
Further passage of sulphur dioxide converts the sulphite to bisulphite:



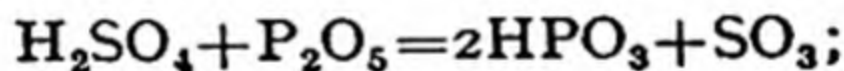
Both salts are white crystalline solids which yield sulphur dioxide on treatment with hydrochloric acid. Like the corresponding potassium and ammonium salts, they are soluble in water. Sulphites of metals other than alkali metals are insoluble in water but dissolve in hydrochloric acid (distinction from sulphates).

Calcium bisulphite, $\text{Ca}(\text{HSO}_3)_2$, is described on p. 344, and *sodium metabisulphite*, $\text{Na}_2\text{S}_2\text{O}_5$, on p. 301.

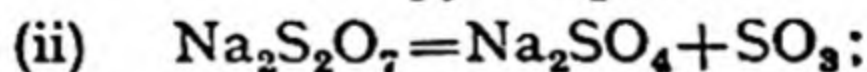
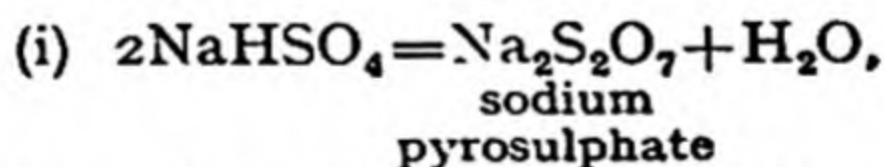
Sulphur trioxide, SO_3 , is formed in small quantity simultaneously with sulphur dioxide, on burning sulphur or a sulphide in air or oxygen. It may be prepared (a) by passing a mixture of sulphur dioxide and oxygen (or air) over a platinum catalyst at about 450° :



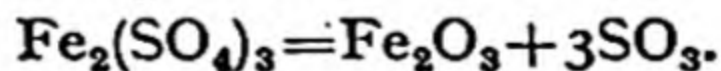
(b) by the action of phosphorus pentoxide on concentrated sulphuric acid:



(c) by heating sodium hydrogen sulphate, NaHSO_4 :

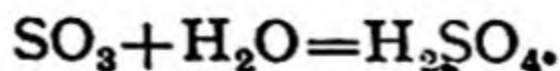


or (d) by heating ferric sulphate:



Sulphur trioxide exists in various modifications. Freshly prepared, it crystallizes in colourless needles (M.P. 17° , B.P. 45°) known as α -sulphur trioxide. On standing, this form spontaneously changes into β -sulphur trioxide, which resembles white asbestos in appearance, and is only slowly attacked by water.

α -Sulphur trioxide readily dissolves in water, combination occurring with great vigour:



Sulphuric acid will itself combine with sulphur trioxide to form *pyrosulphuric acid*, $\text{H}_2\text{S}_2\text{O}_7$. A solution of sulphur trioxide in sulphuric acid is called 'oleum.'

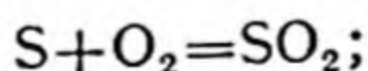
Sulphur trioxide combines directly with basic oxides to form sulphates, often with evolution of so much heat that the mass becomes white hot. It will also combine directly with hydrogen chloride, forming *chlorosulphonic acid*, $\text{Cl.SO}_2\text{OH}$ (p. 523).

MANUFACTURE OF SULPHURIC ACID

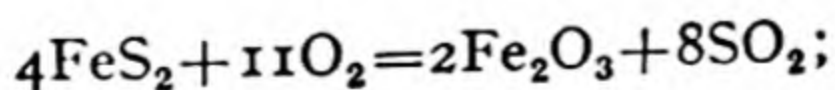
Sulphuric acid is required in almost all the chemical and allied industries (p. 533) and is therefore manufactured on a very large scale; the total annual production amounts to some 10 to 14 million tons. During the eighteenth century, when it first acquired industrial importance, the supply of Nordhausen acid (p. 592) proved insufficient, and sulphuric acid was manufactured by burning a mixture of sulphur and saltpetre and collecting the gaseous products in water. Rapidly increasing demands led to great improvements in procedure, and the *lead-chamber* method was gradually elaborated by ROEBUCK and GARBETT (1746), LA FOLLIE (1774), CLÉMENT and DÉSORMES (1793), GAY-LUSSAC (1830), and GLOVER (1860). Since 1900 the lead-chamber process has had a serious rival in the *contact* process, suggested by PEREGRINE PHILLIPS of Bristol as long ago as 1831, but first successfully operated by R. KNIETSCH of the German firm Badische Anilin-und-Sodafabrik.

Both the lead-chamber and the contact processes are catalytic, and both depend upon the oxidation of sulphur dioxide by atmospheric oxygen. The contact process yields a very pure and very concentrated acid, or oleum if required, but is rather more expensive to run than the lead-chamber process. On the other hand, the lead-chamber acid is less pure than the contact acid and cannot be economically concentrated or converted into oleum. Both processes are consequently employed, but the older method, while still producing the bulk of the world's output, is gradually being displaced by the contact method.

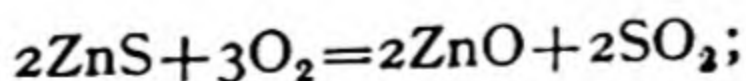
The sulphur dioxide required as raw material is obtained by the combustion in air of either sulphur:



or iron pyrites:



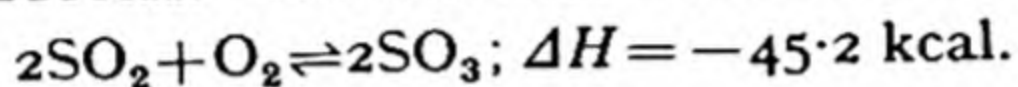
or zinc blende:



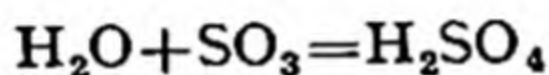
or the 'spent oxide' of the gasworks (p. 393).

The United States and Italy, having large deposits of sulphur, mainly employ the first method; in England and Germany, however, iron pyrites, zinc blende, and spent oxide are generally used, though English manufacturers import a certain amount of sulphur for the purpose. Taking European practice as a whole, the principal source of sulphur dioxide is iron pyrites, which occurs in inexhaustible quantities in the Rio Tinto district of Spain and in smaller deposits in the U.S.S.R., Belgium, France, and Cyprus. Good quality pyrites contains 45 to 50 per cent of sulphur (FeS_2 , when pure, contains 53 per cent), all of which is available on combustion. The heat of combustion is so great that, once ignited, the pyrites continues to burn spontaneously. Zinc blende is poorer in sulphur (33 per cent when pure, usually about 20 per cent commercially) and requires a higher temperature with application of external heat for complete combustion. This disadvantage is offset by the fact that the residual zinc oxide is the chief source of zinc; indeed, the manufacture of sulphuric acid from blende is merely a subsidiary process in the extraction of zinc.

The Contact Process. The essential reaction in this process is:



The sulphur trioxide is then combined with water to form sulphuric acid:



Consideration of the first equation will show that:

(a) The proportion of SO_3 in the equilibrium falls as the temperature rises (LE CHATELIER'S principle). At 450° , the equilibrium mixture contains 98 per cent SO_3 ; at 550° , 85 per cent; at 620° , 70 per cent; at 700° , 40 per cent; and at $1,000^\circ$, practically *nil*.

(b) Conversion of SO_2 into SO_3 will be rendered more nearly complete by using an excess of oxygen. If the sulphur trioxide remains in the state of gas, the equation is:

$$\frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} = K.$$

(c) The forward reaction is accompanied by a decrease in volume and is therefore favoured by increase of pressure (LE CHATELIER).

From these facts the best working conditions would appear to be: comparatively low temperature, increased pressure, and excess of oxygen (air). Unfortunately, however, the time taken to reach equilibrium even at 450° is much too great, while raising the temperature to a point at which the reaction takes place at a satisfactory speed causes the equilibrium proportion of sulphur trioxide to be

negligibly small. It is clear that a solution of the problem lies in the discovery of a catalyst to accelerate the attainment of equilibrium at a temperature which gives a high yield of sulphur trioxide. Two such catalysts are commonly employed, viz. platinum, and vanadium pentoxide or silicate. Platinum is the more efficient, but its catalytic power is rapidly destroyed by the impurities—c.g. arsenious oxide—almost always present in commercial sulphur dioxide; hence careful purification of the gases has to be carried out if platinum is used. Vanadium pentoxide is less efficient, especially with gases in which the proportion of sulphur dioxide is low, but is unaffected by the impurities which 'poison' platinum. For this reason, it is coming into general use, and newly built contact plants are almost all designed for vanadium catalysts.

In the presence of the catalyst, the reaction takes place quickly at 450° , and a 98 per cent yield of SO_3 is obtained. Excess of air is employed, in accordance with the equilibrium law, but increased pressure is found to be unnecessary.

Typical procedure in a modern works using sulphur as the raw material is as follows. Sulphur, from a steel hopper, is fed into a melter heated by superheated steam; any solid impurities are retained by a series of baffles between hopper and melter. The molten sulphur is pumped into a burner consisting of a horizontal cylindrical steel tank lined with heat-resisting firebrick, and meets an incoming stream of air previously dried by passage through 94 per cent sulphuric acid. Complete combustion occurs, and the gases—which contain about 7 per cent of sulphur dioxide, with excess of air and nitrogen—leave the burner at a temperature of about 700° .

This temperature is too high for the catalytic reaction, so the gases are cooled to about 420° – 450° by passing them through two systems of pipes air-cooled by electric fans. They next pass through mechanical filters, where dust is removed, and then enter the catalyst chambers. These chambers, of which there are usually two (in series), contain vanadium pentoxide supported on some inactive material such as asbestos. The rate of flow of the gases is so regulated that the desired temperature (420° – 450°) is maintained, without application of external heat, by the exothermic reaction itself. About 80 per cent of the sulphur dioxide is converted into the trioxide in the first chamber, and the issuing gases are passed through a cooler before entering the second chamber, where the bulk of the catalyst is placed and where the remaining sulphur dioxide is oxidized.

After a further cooling, the gas mixture (SO_3 , O_2 , N_2) is passed up a tower down which cold 98–99 per cent sulphuric acid is sprayed; this absorbs the sulphur trioxide to form oleum. The acid leaving the absorber is diluted with water to 98–99 per cent, and sufficient of

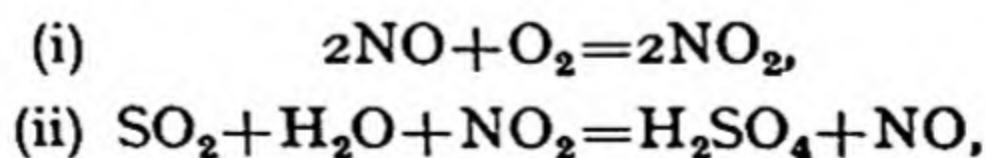
it is recirculated to the absorber. The rest is run off for storage and sale.

Such a plant can be worked by a single operator, and may produce as much as 100 tons of 98 per cent sulphuric acid daily. The average power consumption per ton of acid is 36 kilowatt-hours, which, at a cost of $\frac{1}{4}d.$ per unit, is equivalent to $9d.$ Oleum of various concentrations up to 25 per cent SO_3 may be obtained by absorbing the sulphur trioxide in concentrated sulphuric acid until the required concentration is reached.

Where pyrites or other sulphide-mineral is the source of the sulphur dioxide, and platinum is used as catalyst, the gases leaving the burners are passed between highly charged conductors, which cause electrostatic precipitation of solid particles (As_2O_3), etc. (LODGE-COTTRELL system). Alternatively they are washed with a spray of water, and in both cases are afterwards dried with sulphuric acid. They then pass over the catalyst at $420^\circ\text{--}450^\circ$. In some works, ferric oxide at $600^\circ\text{--}700^\circ$ is employed as a preliminary

catalyst; this effects oxidation of about two-thirds of the sulphur dioxide and has the advantage that no purification of the gases is necessary, since, although the efficiency of the ferric oxide is gradually impaired by the absorption of the impurities, it is so cheap that it can be replaced economically as often as required. The mixture of gases leaving the ferric oxide chamber is sufficiently pure for the remaining conversion to be carried out with a platinum catalyst.

The Lead - Chamber Process. In the lead - chamber process, oxidation of the sulphur dioxide is effected by oxides of nitrogen in the presence of water. The oxides are afterwards recovered and may therefore be regarded as having acted catalytically. The reactions involved are usually stated to be:



which would be an admirably simple explanation, but suffers from the fact that the second reaction does not occur under working conditions.

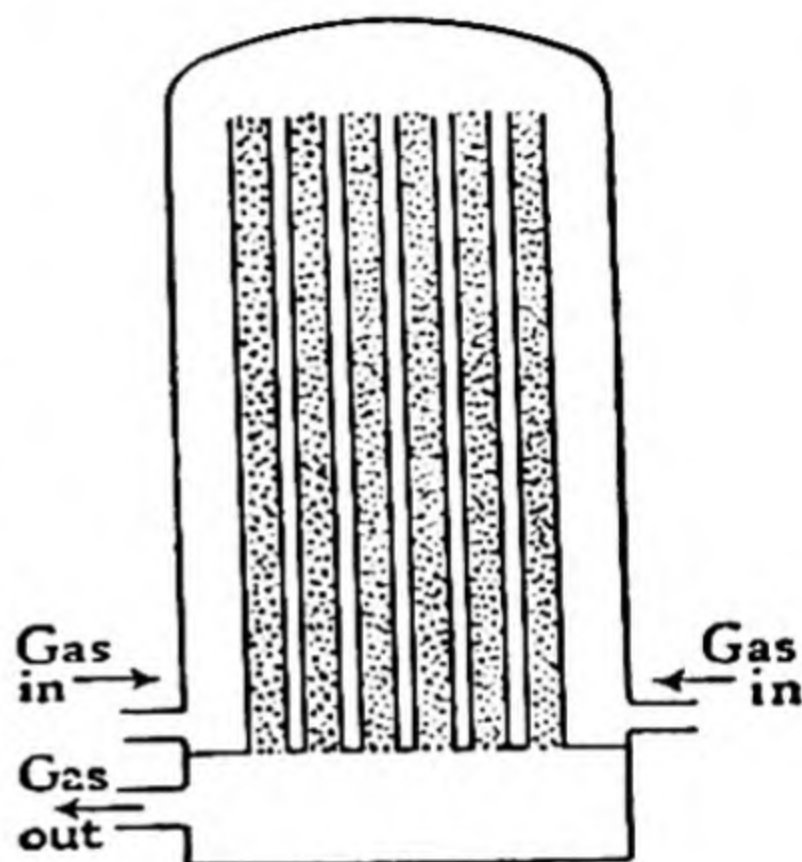
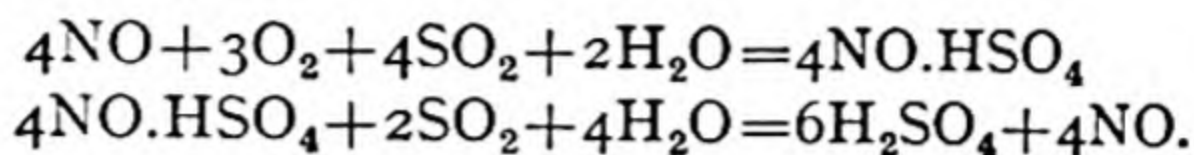


FIG. 96. CONTACT TOWER

A second theory, less open to objection, suggests that *nitrososulphuric acid*, NO.HSO_4 ('chamber-crystals'), is alternately formed and decomposed:



It is known that nitrososulphuric acid is formed if the supply of water is inadequate, but it does not certainly follow that it is formed when the plant is working properly.

A diagram of a 'lead-chamber' works is given in Fig. 97. Perhaps the most surprising point about it is that there are no lead chambers; actually the name is a survival from the time when enormous

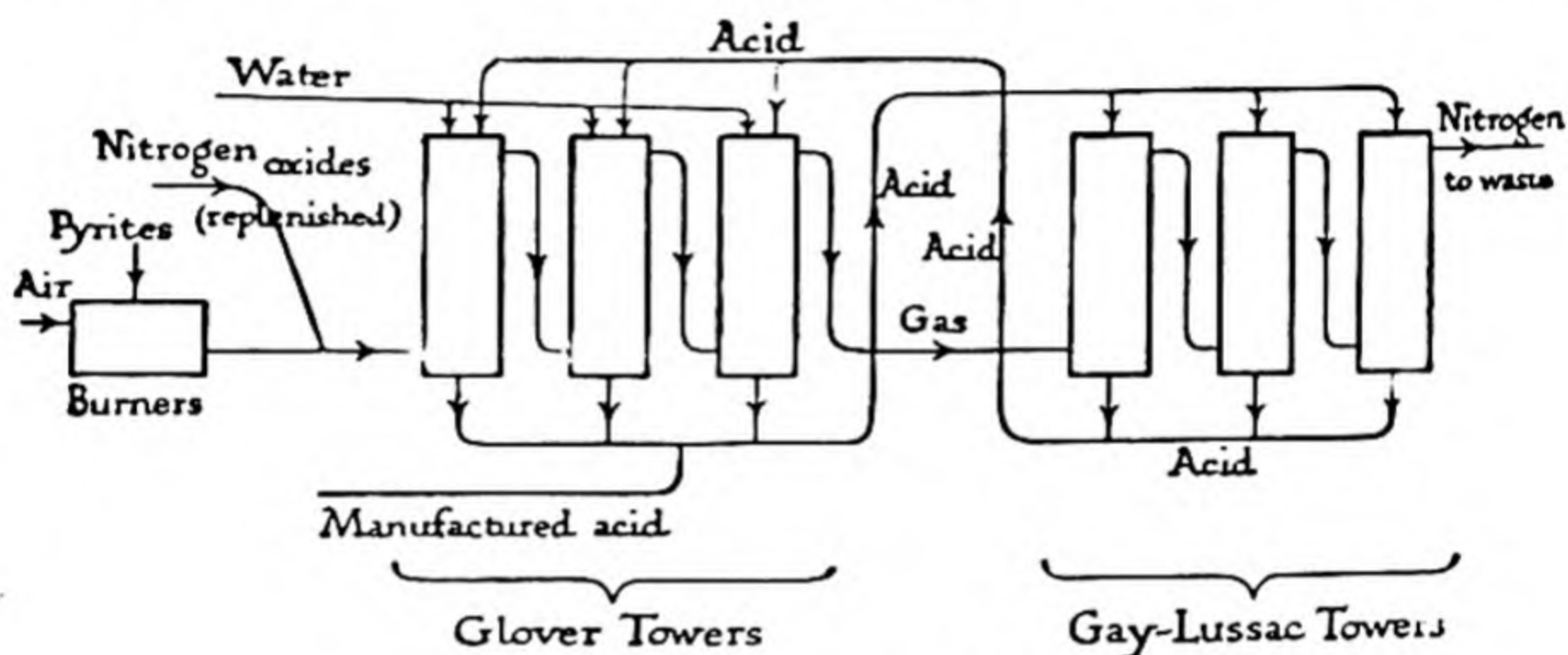


FIG. 97. CHAMBER PROCESS

wooden chambers lined with lead formed the most conspicuous part of the plant. These may yet be seen where old plants are still functioning, but new plants dispense with them entirely.

Air, in excess, is blown over heated pyrites, and the mixture of sulphur dioxide, oxygen, and nitrogen emerging from the burners takes up a small quantity of oxides of nitrogen (prepared by the catalytic oxidation of ammonia) before entering the first of three or four GLOVER * towers. Here the gases meet a downward-flowing stream of 65–70 per cent sulphuric acid containing dissolved oxides of nitrogen, and here occur the reactions resulting in the formation of sulphuric acid. Water is run in at the tops of the Glover towers, since the acid (containing the oxides of nitrogen) supplied to them is much more concentrated, and water is therefore necessary for reaction with the gases.

Acid of about 78 per cent strength runs from the bottom of the

* Mr. N. F. Newbury informs me that the first of such towers was built by JOHN GLOVER (1817–1902) in 1859 at the Washington Chemical Works near Durham.

Glover towers, and by the time the gases leave the last of them, all the sulphur dioxide has been converted into sulphuric acid. Most of the 78 per cent acid is removed for sale, and the rest is pumped to the top of the GAY-LUSSAC towers, down which it flows. As the gases from the last Glover tower pass up the Gay-Lussac towers, the oxides of nitrogen dissolve in the descending acid, which is returned to the tops of the Glover towers; the residual nitrogen is delivered as waste to the chimney-stack. Most of the oxides of nitrogen is thus recovered and used again; slight losses are replenished as previously indicated.

The Glover towers are lined with pure lead and both they and the Gay-Lussac towers are packed with earthenware tiles, flints, coke, or other acid-resisting material, to expose to the gases as large a surface as possible of the acids. The concentration of acid in the Glover towers is not allowed to rise above 78 per cent H_2SO_4 , since more concentrated acid readily attacks lead.

The 'chamber acid' produced in this way is usually sold as such, being already sufficiently concentrated for several purposes, e.g. the manufacture of 'superphosphate' (p. 345) and other fertilizers, and the manufacture of hydrogen chloride from common salt (p. 548). If acid of higher concentration is required, it is less expensive to buy contact acid, though chamber acid can be concentrated by spraying it through hot furnace gases (GAILLARD method) and in other ways.

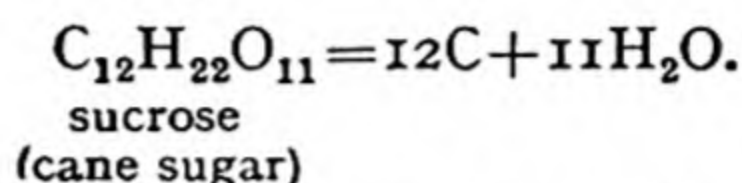
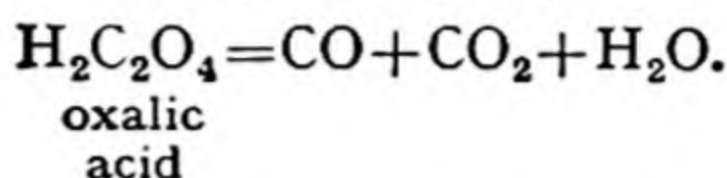
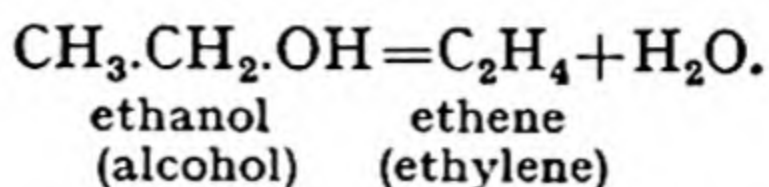
Uses of sulphuric acid. As just mentioned, sulphuric acid is used in the manufacture of 'superphosphate,' though the consumption for this purpose is now declining. It is also used in the refinement of petroleum, the manufacture of chemicals, paints, and explosives, as the electrolyte in accumulators, and in cleaning iron sheet for tinning and galvanizing. Of minor applications it has legion.

Properties of sulphuric acid. Pure anhydrous sulphuric acid is a heavy, colourless, oily liquid which, at temperatures slightly below average room temperature, solidifies to a white crystalline solid (M.P. 10.5°). The specific gravity of the pure liquid acid at 20° is 1.834. On heating it loses sulphur trioxide until the concentration of the remaining liquid is 98.3 per cent H_2SO_4 ; this liquid is a constant-boiling mixture and boils at 330° (760 mm.). If dilute sulphuric acid is distilled, the concentration of the solution left in the distilling-flask rises until the constant-boiling mixture is formed.

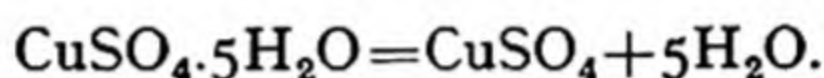
Sulphuric acid is remarkable for its excessive avidity for water. When the concentrated acid is added to water, the temperature rises very rapidly, sometimes by more than 100° . From aqueous sulphuric acid it is possible to isolate (by freezing) three distinct hydrates, viz. $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$, and $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$.

Besides combining with liquid water, concentrated sulphuric acid

will also dehydrate many compounds which contain hydrogen and oxygen; e.g.:

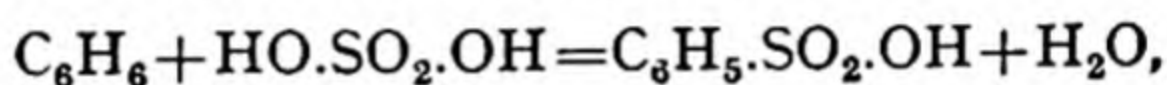


When heated with crystalline hydrates, it frequently dehydrates them:



In all these reactions the water is taken up by the sulphuric acid.

Anhydrous sulphuric acid behaves rather as a *sulphonating agent* and *oxidizing agent* than as an acid. Thus when heated with benzene it yields *benzene-sulphonic acid*, $\text{C}_6\text{H}_5\text{SO}_3\text{H}$:



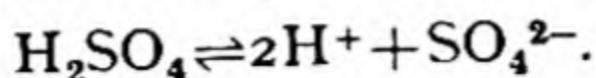
while copper is oxidized to cupric sulphate, cupric sulphide, and cuprous sulphide (p. 525). When acting as an oxidizing agent, the acid is reduced to sulphur dioxide, or even further, viz. to sulphur and hydrogen sulphide.

In aqueous solution, sulphuric acid behaves as a strong acid, and shows the normal properties of such substances. It is dibasic, and forms two series of salts, viz. the *acid sulphates* (bisulphates or hydrogen sulphates) and the *normal sulphates*. Most sulphates are soluble in water; the chief insoluble or slightly soluble ones are Hg_2SO_4 (mercurous sulphate), PbSO_4 , Ag_2SO_4 , BaSO_4 , SrSO_4 , CaSO_4 .

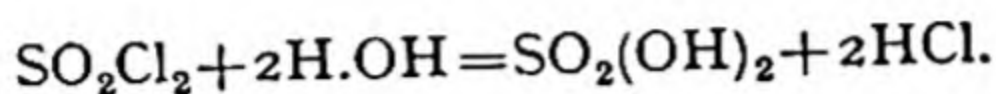
Zinc sulphate, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, ferrous sulphate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, and copper sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, are known respectively as white vitriol, green vitriol, and blue vitriol. Since sulphuric acid may be obtained by heating any of these salts to a sufficiently high temperature (and was indeed formerly manufactured in this way, p. 592), it is popularly called 'oil of vitriol.'

Constitution of sulphuric acid. The composition of sulphur trioxide was elegantly demonstrated by Gay-Lussac, who showed that the gaseous product from the ignition of aluminium sulphate (used in the form of 'burnt alum,' $\text{KAl}(\text{SO}_4)_2$) consisted of sulphur dioxide and oxygen in the volume proportions 2 : 1. By Avogadro's principle, the empirical formula of sulphur trioxide must be SO_3 . 80 gm. of sulphur trioxide combine with 18 gm. of water, yielding

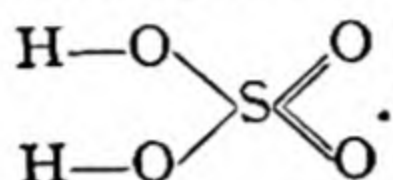
98 gm. of sulphuric acid; hence the empirical formula of sulphuric acid is H_2SO_4 . In solution, sulphuric acid produces *three* ions, a fact which indicates that its empirical formula is also its molecular formula:



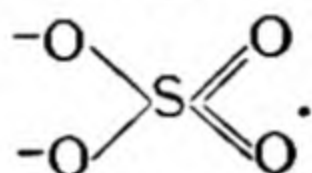
The synthesis of sulphuric acid by the hydrolysis of sulphuryl chloride, SO_2Cl_2 , shows that the structure of the acid is probably $\text{SO}_2(\text{OH})_2$:



Assuming sulphur to exert a valency of VI, as in sulphur hexafluoride, the formula of sulphuric acid could be written:

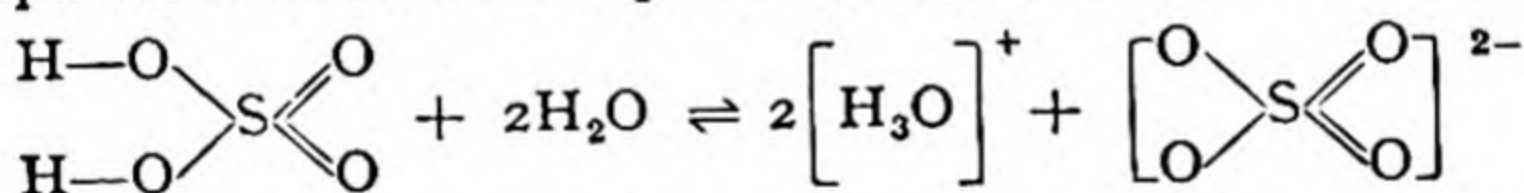


This formula is supported by modern methods of X-ray examination, which have shown that the sulphate ion, SO_4^{2-} , present in sulphates, can be regarded as having the constitution

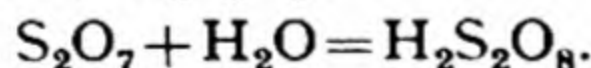


These methods have not yet been directly applied to the acid itself.

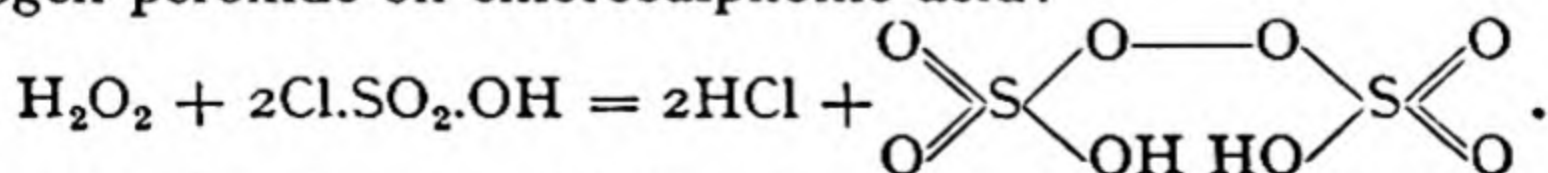
Sulphuric acid in dilute aqueous solution ionizes as follows:



Sulphur heptoxide, S_2O_7 , is an ill-defined substance said to be formed when a mixture of sulphur trioxide and oxygen is subjected to the silent electric discharge. It is believed to be the anhydride of *peroxydisulphuric acid*, $\text{H}_2\text{S}_2\text{O}_8$:



Peroxydisulphuric acid, persulphuric acid, $\text{H}_2\text{S}_2\text{O}_8$, can be prepared as a colourless crystalline solid (M.P. 60°) by the action of hydrogen peroxide on chlorosulphonic acid:



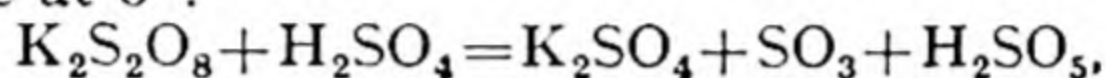
It may also be prepared in solution by the electrolysis of well-cooled 40–50 per cent sulphuric acid.

Peroxydisulphuric acid is an oxidizing agent and a strong dibasic acid. The *persulphates*, e.g. potassium persulphate, $\text{K}_2\text{S}_2\text{O}_8$, and ammonium persulphate, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, are prepared electrolytically

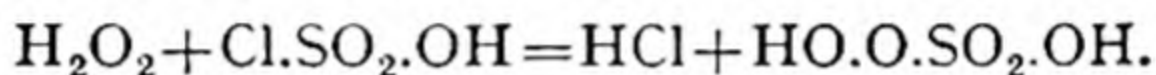
and are used in industrial chemistry as oxidizers. Ammonium persulphate was used in the manufacture of hydrogen peroxide (p. 506). When treated with nitric acid it yields ozonized oxygen.

Sulphur tetroxide, SO_4 , is a white solid, M.P. 0° , obtained when a mixture of sulphur dioxide with excess of oxygen is subjected to the glow electric discharge at low pressure (less than 1 mm.). It is a powerful oxidizing agent, converting manganous salts into permanganates and aniline into nitrobenzene. From its formula it appears to be the anhydride of *peroxymonosulphuric acid*, H_2SO_5 , but this acid is not formed when the tetroxide is dissolved in water.

Peroxymonosulphuric acid, Caro's acid, H_2SO_5 , can be prepared by the action of concentrated sulphuric acid on potassium peroxydisulphate at 0° :



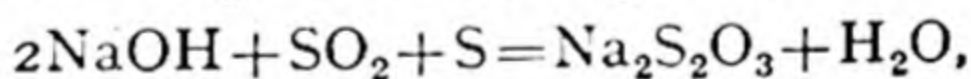
or by the interaction of chlorosulphonic acid and hydrogen peroxide in equimolecular proportions:



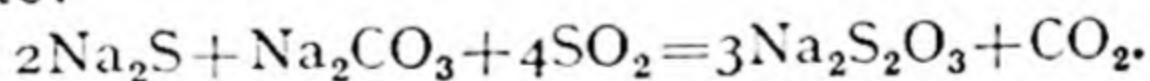
Like peroxydisulphuric acid, it is a colourless crystalline solid (M.P. 45°) with strong oxidizing powers: it is monobasic.

Thiosulphurous acid, $\text{H}_2\text{S}_2\text{O}_2$, and **thiosulphuric acid**, $\text{H}_2\text{S}_2\text{O}_3$, are both unknown, but thiosulphites and thiosulphates have been prepared, and *sodium thiosulphate*, $\text{Na}_2\text{S}_2\text{O}_3$, is an important salt in both pure and applied chemistry. It may be regarded as sodium sulphate, Na_2SO_4 , in which one oxygen atom has been replaced by sulphur; hence the name *thio*-sulphate (Greek: *theion*, sulphur).

Sodium thiosulphate is manufactured by passing sulphur dioxide into a suspension of sulphur in boiling caustic soda solution:

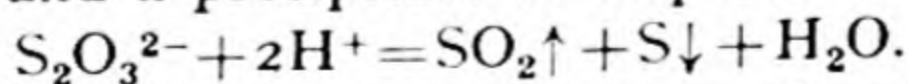


or by blowing sulphur dioxide into a hot solution of sodium sulphide and carbonate:

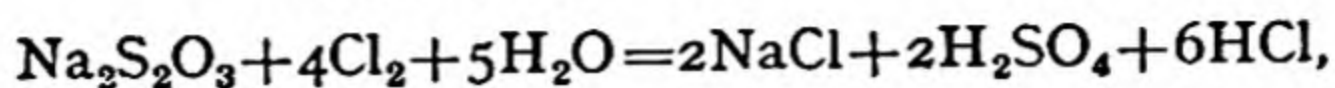


The salt separates out from the solutions, on cooling, in the form of colourless crystals of the *pentahydrate*, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. If these are heated they melt to a colourless solution, which when cooled in the absence of dust and agitation very frequently becomes supersaturated.

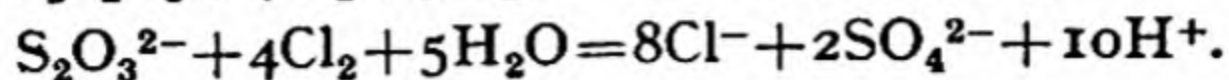
Dilute acids react with sodium thiosulphate in the cold, yielding sulphur dioxide and a precipitate of sulphur:



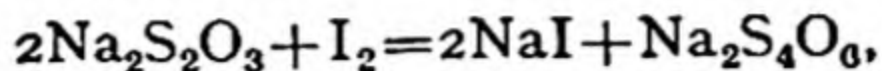
Sodium thiosulphate is used in photography to dissolve silver halides (p. 330); in photographic parlance it is 'hypo.' It is also employed industrially as an antichlor, since it reacts with chlorine as follows:



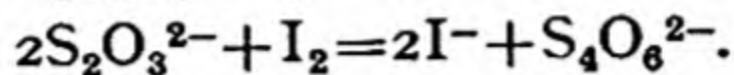
or



Its reaction with iodine is different, and results in the formation of *sodium tetrathionate*, $\text{Na}_2\text{S}_4\text{O}_6$:

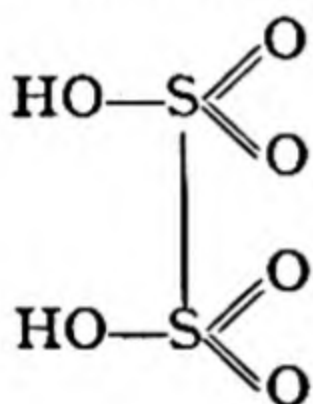


or

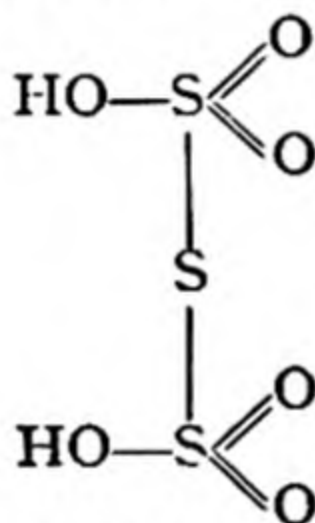


This reaction is familiar from its use in volumetric analysis. The end-point is ascertained by the addition of fresh starch solution just before the yellow colour of the iodine vanishes. The disappearance of the deep-blue colour of the iodine-starch 'compound' on addition of a few further drops of thiosulphate is very sharp indeed.

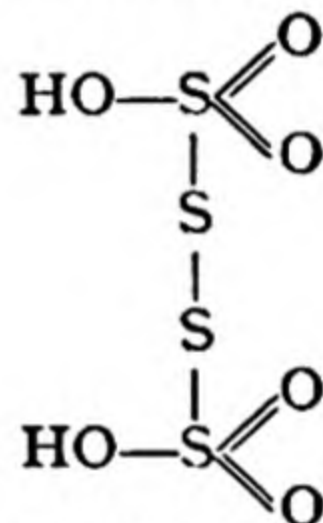
Thionic acids. Sodium tetrathionate is the sodium salt of tetrathionic acid, $\text{H}_2\text{S}_4\text{O}_6$. Other similar acids are known: they have the general formula $\text{H}_2\text{S}_n\text{O}_6$, where $n=2, 3, 4, 5$, or 6 , and are known as *thionic acids*. Their constitutions are as follows:



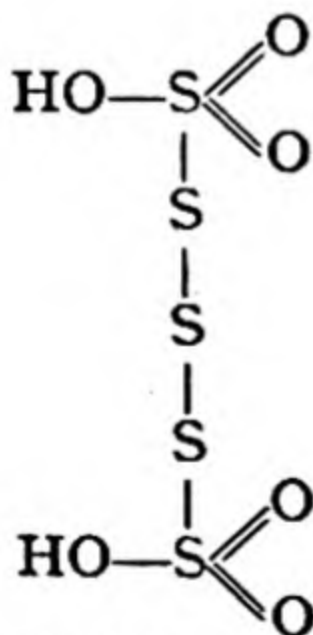
di-thionic acid



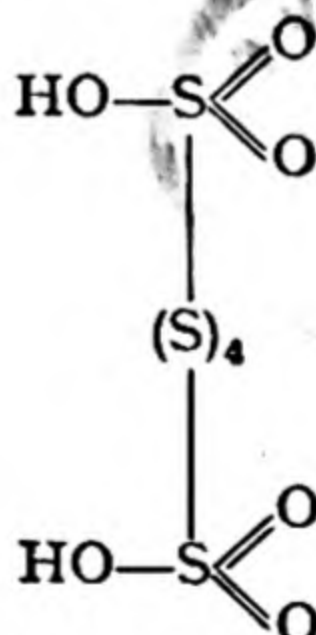
tri-thionic acid



tetra-thionic acid



penta-thionic acid



hexa-thionic acid

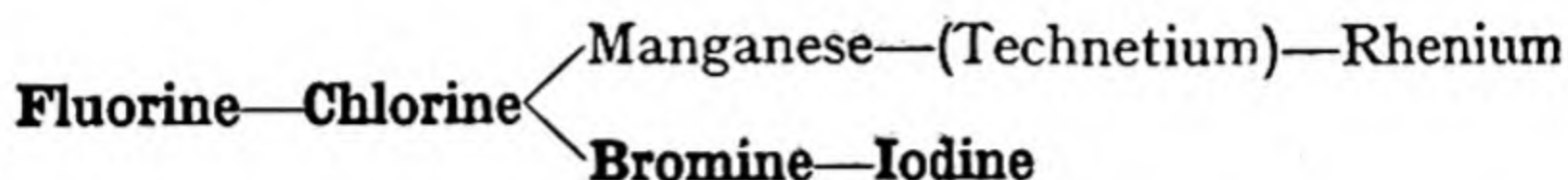
COMPARATIVE EXERCISES

1. Make an outline comparative table for oxygen and sulphur.
2. Make a more detailed table to show the resemblances and differences between oxides and sulphides.

CHAPTER XXX

GROUP VII

THE HALOGENS



The Halogens. The typical elements fluorine and chlorine form a very well defined family with the elements of Sub-group B, bromine and iodine. Since chlorides, bromides, and iodides are typical solutes of sea-water, the family as a whole is known as the *halogen* family (Greek, salt-producer). Manganese is very different from the halogens, though it closely resembles rhenium. It also has similarities to chromium, iron, cobalt, and nickel (Chapter XXXI).

FLUORINE, F

Atomic number: 9. *Atomic weight:* 19.00. *Density* ($H=1$): 18.8.
Melting-point: -223° . *Boiling-point:* -182° .

History. The first recorded occasion on which a compound of fluorine was employed seems to have been in 1670, when SCHWAN-HARDT etched glass with a mixture of fluor-spar (CaF_2) and sulphuric acid. In 1771 SCHEELE prepared an impure specimen of hydrofluoric acid, and recognized that fluor-spar was a salt of this acid with lime. AMPÈRE suggested in 1810 that hydrofluoric acid might be a compound of hydrogen with an unknown element, *fluorine*, analogous to chlorine. GAY-LUSSAC and THENARD had previously (1809) carried out a thorough investigation of the acid, which they believed to be the oxide of a new radical; but after DAVY (1810) had shown that chlorine is an element, the similarity between hydrochloric acid and hydrofluoric acid made it extremely probable that AMPÈRE'S suggestion was correct. In spite of great ingenuity and perseverance, however, it proved impossible to isolate fluorine until 1886, when MOISSAN triumphed over great experimental difficulties.

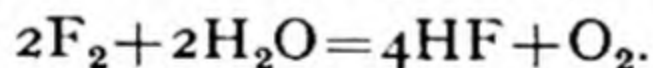
Occurrence. Although fluorine is fairly abundant and widely distributed, the only important minerals containing it are *fluor-spar* ('Derbyshire spar' or 'Blue John'), i.e. calcium fluoride, CaF_2 ;

cryolite, or sodium fluo-aluminate, Na_3AlF_6 ; and *fluorapatite*, $\text{CaF}_2 \cdot 3\text{Ca}_3(\text{PO}_4)_2$. The principal deposits of cryolite ('ice-stone') occur in Greenland.

In smaller quantities, fluorine is found in plant ashes, in the enamel of teeth, and in many other unexpected places. It forms about 0.03 per cent of the earth's crust, chlorine forming about 0.19 per cent.

Preparation. Owing to its very great chemical activity and to the excessively poisonous nature of its chief compound hydrogen fluoride, the isolation of fluorine proved a very difficult task. The story of its final achievement by MOISSAN is one of the epics of chemistry. After repeated and disheartening failures, extending over many years and costing a great deal of money, this brilliant professor at the *École de Pharmacie* in Paris obtained the first bubbles of the new element on 26th June 1886. He at once reported his success to the Academy of Sciences, which appointed a committee to investigate and confirm the discovery. Needless to say, the apparatus obstinately refused to work before the distinguished investigators; but on the following day it behaved admirably, and MOISSAN had the intense satisfaction of demonstrating the preparation of fluorine to men who could properly appreciate the difficulties that he had had to overcome.

In attacking the problem, MOISSAN had rightly surmised that an electrolytic process would be the only means of releasing elementary fluorine. Electrolysis of a fluoride in *aqueous* solution could not be expected to succeed, since, apart from the very high discharge potential of fluoride ion, fluorine vigorously attacks water:



MOISSAN accordingly chose as solvent hydrogen fluoride (B.P. 19°), the only material immune from attack and liquid at ordinary temperature known to chemists at the time of his experiments. As electrolyte he used potassium hydrogen fluoride, KHF_2 , the action at the anode being:



Upon electrolysing such a solution in a U-tube made of an alloy of platinum and iridium, with electrodes of the same alloy, the whole apparatus being cooled to about -23° in a bath of methyl chloride, he obtained hydrogen at the cathode and a pale greenish-yellow gas at the anode.

Since the days of MOISSAN, easier methods of preparing fluorine have been discovered. The most convenient consists in the electrolysis of a molten mixture of potassium hydrogen fluoride and hydrogen fluoride in an electrically heated vessel of steel, which serves as cathode. The anode is made of graphite and is sur-

rounded by a perforated diaphragm of Monel metal. The electrolysis is carried out with a current of 10 to 20 amperes at 10 to 20 volts, and the temperature is maintained at about 100° .

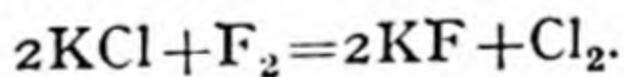
For carrying out experiments on fluorine, copper vessels and tubes may be used, since the metal quickly becomes coated with a film of copper fluoride which protects it from further corrosion.

Properties. Fluorine, the most reactive and the most strongly electronegative of all the elements, is a pale yellow gas which can be condensed to a canary-yellow liquid boiling at -182° ; the liquid on further cooling solidifies to a pale yellow crystalline mass melting at -223° . At still lower temperatures, the solid becomes colourless.

Fluorine has a moderately pungent smell and produces very severe wounds if allowed to come into contact with the flesh; a characteristic feature of these wounds is that they tend to grow worse with lapse of time unless very skilfully treated, or unless the affected portions of flesh are actually cut out.

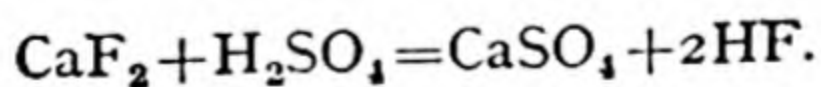
Fluorine reacts, often with considerable violence, with all elements except the inert gases, oxygen and nitrogen. Even the last two elements, however, form fluorides by indirect means, and in 1928 RUFF and his collaborators observed the direct combination of fluorine with chlorine at a temperature of 250° . Carbon is only slowly attacked by fluorine at ordinary temperatures, unless finely divided. Hydrogen and even liquid fluorine (-182°) combine explosively to form hydrogen fluoride.

Fluorine attacks water vigorously, forming hydrogen fluoride, oxygen, ozone, hydrogen peroxide, and possibly traces of the gaseous oxide of fluorine, F_2O (q.v.). It also attacks organic compounds—many of which ignite spontaneously in it—and moist glass. It reacts with chlorides, liberating chlorine, e.g.:



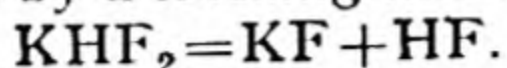
With potassium hydroxide solution, fluorine produces a variety of products, stated to include potassium superoxide, KO_2 .

Hydrogen fluoride, HF . As already mentioned, hydrogen and fluorine react together extremely energetically. Hydrogen fluoride is more conveniently prepared by the distillation of calcium fluoride with concentrated sulphuric acid in lead, or preferably platinum, apparatus; glass must not be used, since hydrogen fluoride attacks it:



Hydrogen fluoride comes off as a colourless gas, which may be condensed to a colourless liquid in a receiver surrounded by a freezing-mixture, or dissolved in water to form the aqueous solution (hydrofluoric acid).

The most suitable method of obtaining the anhydrous substance is to distil well-dried potassium hydrogen fluoride, KHF_2 , in a platinum distillation apparatus and to collect the product in a platinum receiver cooled by a freezing-mixture:



Hydrogen fluoride is a colourless liquid boiling at 19.5° and freezing to a colourless crystalline solid at -83° . Like fluorine, it is a very dangerous substance, producing severe burns on the flesh, and often proving fatal if inhaled in more than slight traces. The *greatest possible care* is necessary in working with it. It fumes in moist air, and is readily soluble in water, with which it forms a constant-boiling mixture (B.P. 120°) containing 36–37 per cent of hydrogen fluoride.

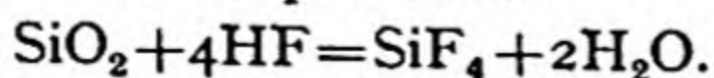
The constitution of the salt KHF_2 has been much discussed. The problem really concerns the anion $(\text{HF}_2)^-$, which is now known to be a linear ion $(\text{FHF})^-$. The accepted assumption is that the binding is largely, if not wholly, electrostatic $(\text{F}^-\cdot\text{H}^+\cdot\text{F}^-)^-$, and thus provides another example of 'hydrogen bonds,' discussed on p. 118.

Vapour density measurements show that, at temperatures immediately above its boiling-point, hydrogen fluoride is highly associated. On rise of temperature, dissociation rapidly occurs, and the gas becomes entirely HF at 65° . HF molecules will readily combine with fluorides of both metals and non-metals. Thus *anhydrous* HF will unite with the fluorides KF, NaF, and NH_4F , giving hydrofluorides MHF_2 , discussed above; *aqueous* HF dissolves aluminium fluoride to form *fluoaluminic acid*, H_3AlF_6 ; and combines with boron trifluoride and silicon tetrafluoride to form *fluoboric acid*, HBF_4 , and *fluosilicic acid*, H_2SiF_6 , respectively. Well-known salts of these acids are: Na_3AlF_6 , sodium fluoaluminate (cryolite), KBF_4 , potassium fluoborate, and K_2SiF_6 , potassium fluosilicate. Such actions of HF may be compared with the actions of water upon acid anhydrides to give oxy-acids.

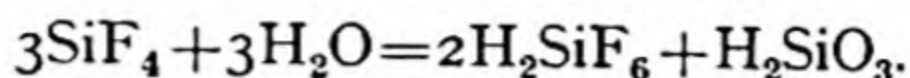
A solution of hydrogen fluoride is known as hydrofluoric acid. This acid, unlike hydrochloric acid, is only moderately strong. In concentrated solution, association occurs, and the acid $\text{H}[\text{HF}_2]$ is considerably stronger than HF.

Hydrofluoric acid readily attacks glass, and is therefore used in glass-etching. The glass is coated in paraffin wax, and the design is scratched on it with a pointed stylus, so as to remove the wax in the appropriate places. The object is then exposed to aqueous or gaseous hydrogen fluoride for some hours, after which the wax is melted or dissolved off, and the pattern is found to be etched on the glass.

The essential reaction in the process is:



In the presence of moisture, silicon tetrafluoride is hydrolysed to fluosilicic (silicofluoric) acid and silicic acid:



Among the FLUORIDES, *silver fluoride*, AgF , is yellow in colour, and very soluble in water, while silver chloride, bromide, and iodide are insoluble; and *calcium fluoride*, CaF_2 , is similarly noteworthy as being insoluble in water, while calcium chloride, bromide, and iodide are very soluble. *Mercurous fluoride*, Hg_2F_2 , resembles silver fluoride, and is soluble in water. Mixed chlorides and fluorides of carbon, e.g. *difluoro-dichloro-methane*, CF_2Cl_2 , and *tetrafluoro-dichloro-ethane*, $\text{CFCl}_2.\text{CF}_3$, are commonly used as the working liquids in refrigerators. The former boils at -30° and the latter at 3.5° , giving colourless vapours which do not corrode metals.

Oxygen fluorides or *fluorine oxides* of the formulae F_2O and F_2O_2 are known. Fluorine monoxide, F_2O , is a colourless, extremely poisonous, non-explosive gas made by bubbling fluorine into cold dilute sodium hydroxide solution. No oxy-acids of fluorine, or salts of such acids, have yet been obtained.

Within the last few years, intensive research on fluorine compounds has been carried out, owing to the very useful technical and industrial properties many of these substances have been found to possess, e.g. as plastics, insulators, lubricants, and fire-extinguishers.

CHLORINE, Cl

Atomic number: 17. *Atomic weight:* 35.457. *Relative density* ($H=1$): 35.98 (N.T.P.). *Melting-point:* -104° . *Boiling-point:* -34° .

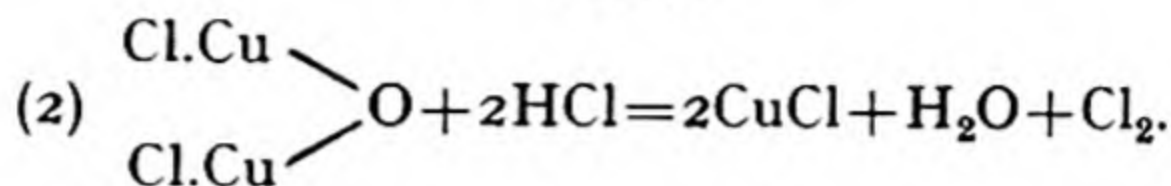
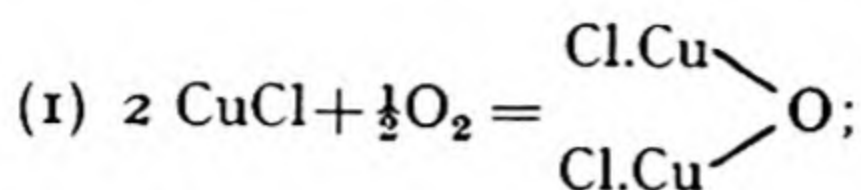
History. Chlorine was one of the numerous gases discovered during the age of Pneumatic Chemistry (p. 14); it was first isolated in 1774 by SCHEELE. Scheele heated muriatic acid (HCl) with pyrolusite (MnO_2), and obtained a poisonous gas which he regarded as muriatic acid from which phlogiston (p. 6) had been removed. He accordingly called it *dephlogisticated muriatic acid air*. When the phlogiston theory was overthrown, the new gas was considered to be a compound of oxygen and muriatic acid; hence it was renamed *oxymuriatic acid*. DAVY, however, in 1810 reported that, although he had heated sulphur, charcoal, and several metals—including sodium—in oxymuriatic acid, he had never succeeded in obtaining either oxygen or any known oxygen compound from it. In accordance with the principle laid down by BOYLE (p. 6), therefore, he maintained that it must be ranked as an element, suggesting the name *chlorine* for it on account of its greenish-yellow colour (Greek *chlōros*, greenish-yellow).

Occurrence. Like other elements of great chemical affinity, chlorine is not found free in nature. Its compounds, however, are abundant and widespread, the chief of them being *sodium chloride*, or common salt, NaCl (p. 295). *Magnesium chloride*, $MgCl_2$, and *potassium chloride*, KCl, occur in sea-water, and, in the solid state, in saline deposits in various parts of the world. At Stassfurt, in Germany, for example, the salt-beds contain large quantities of *sylvine* (KCl) and *carnallite* ($KCl \cdot MgCl_2 \cdot 6H_2O$). *Silver chloride*, AgCl, occurs naturally as *horn silver*, and a *basic copper chloride*, $CuCl_2 \cdot 3Cu(OH)_2$, as *atacamite*. Volcanic gases often contain small quantities of *hydrogen chloride*.

Chlorine is essential to all forms of life, which usually absorb it as sodium chloride. The aqueous fluid of the blood contains sodium chloride in solution.

Manufacture. Chlorine has important industrial applications and is therefore prepared on a large scale. The old WELDON process is now obsolete; it consisted in heating manganese dioxide with concentrated hydrochloric acid, and recovering the dioxide from the residual solution of manganous chloride by atmospheric oxidation in the presence of lime. The DEACON process, however, has recently been revived. Here hydrogen chloride is oxidized by air at 400° with copper chloride as catalyst. The chlorine obtained is, of

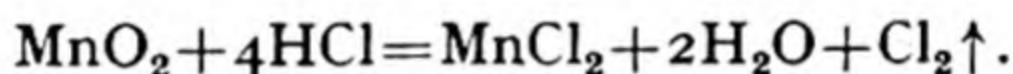
course, diluted with nitrogen. The catalysis is explained by the stages:



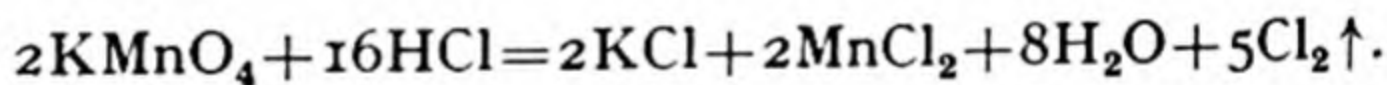
At the present day chlorine is prepared mainly by the *electrolysis of brine* as described on p. 290. It is carefully dried by passage through concentrated sulphuric acid, liquefied, and transported as liquid chlorine in steel cylinders.

Laboratory Preparation. In the laboratory, chlorine is conveniently obtained from a cylinder. It can, however, be prepared in the following ways:

- (a) By heating manganese dioxide with concentrated hydrochloric acid:



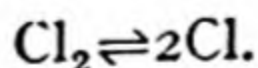
- (b) By dropping concentrated hydrochloric acid upon potassium permanganate crystals. No heat is necessary.



- (c) By dropping a dilute acid upon bleaching-powder (p. 342).

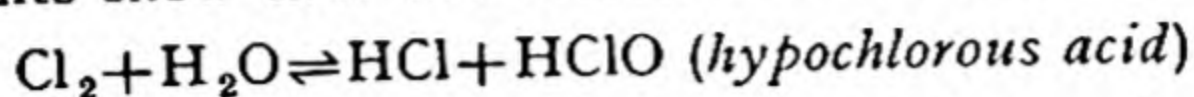
The gas prepared in any of these ways may be washed by bubbling it through a little water, dried with concentrated sulphuric acid, and collected by air displacement (since it attacks mercury, is much denser than air, and is moderately soluble in water).

Properties. Chlorine is a poisonous, greenish-yellow gas with a pungent and suffocating smell. It is some $2\frac{1}{2}$ times as dense as air. Its vapour density at N.T.P., viz. 35.98, is higher than corresponds (35.457) to the formula Cl_2 , since near its boiling-point, -34° , the gas is 'imperfect' (p. 61). On heating, the value gradually falls, becoming 35.457 at about 120° . Further rise of temperature causes very little dissociation up to about $1,300^\circ$ – $1,400^\circ$, after which the dissociation of the diatomic molecules into single atoms becomes considerable:

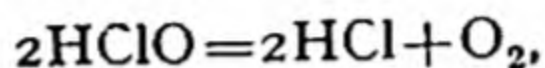


The critical temperature (p. 64) of chlorine is 146° , hence the gas can be liquefied by pressure alone (about 6 atmospheres) at ordinary temperatures. It forms a golden-yellow liquid (B.P. -34°) immiscible with water and much less active than the gaseous element. It freezes at -104° to a pale yellow crystalline solid.

Chlorine is somewhat soluble in water, the solubility at 15° being about 8.5 gm. per litre. The solution is called *chlorine water*, is yellowish in colour, and smells strongly of chlorine. Conductivity measurements show that the reversible reaction:



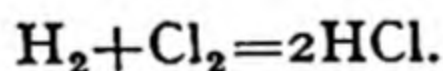
occurs, to an extent varying with the conditions. In a saturated solution at 0° the hydrolysis is about 32 per cent. Hypochlorous acid is an unstable substance (especially in the presence of light), readily decomposing into oxygen and hydrochloric acid:



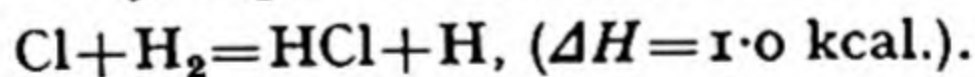
so that chlorine water is gradually converted into hydrochloric acid with evolution of oxygen. PEDLER showed that the decomposition occurs more quickly in dilute chlorine water than in more concentrated solutions.

If chlorine is passed into ice-cold water, yellowish crystals of *chlorine hydrate* separate out. The composition of this substance is uncertain, FARADAY giving it as $\text{Cl}_2 \cdot 10\text{H}_2\text{O}$, ROOZEBOOM as $\text{Cl}_2 \cdot 8\text{H}_2\text{O}$, the latter being the more probable. The crystals rapidly decompose into chlorine and water when heated, a fact employed by Faraday to liquefy the gas. He warmed chlorine hydrate in one limb of a bent sealed glass tube and liquid chlorine collected in the other limb, which was surrounded by a freezing-mixture.

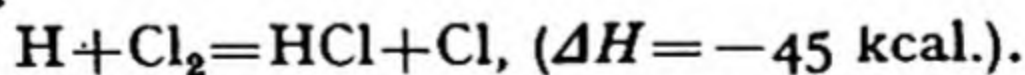
When hydrogen and chlorine are mixed in the dark at ordinary temperature, no reaction occurs. In diffused daylight the gases combine slowly to form hydrogen chloride, and the reaction takes place explosively in bright light (e.g. sunlight or the light of burning magnesium):



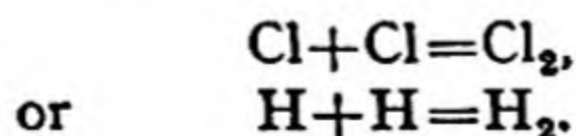
A molecule of chlorine absorbs a unit (*quantum*) of light energy which causes it to split up into individual atoms. These atoms are able to react with hydrogen molecules as follows:



and the hydrogen atoms react with chlorine molecules to form more chlorine atoms:



Once the chain is started it goes on until broken by one of the reactions:

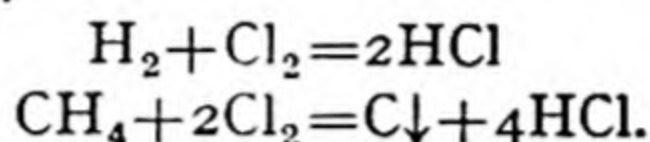


Such reactions occur readily on the walls of the containing vessel. It has been found that one activated chlorine atom (i.e. one quantum

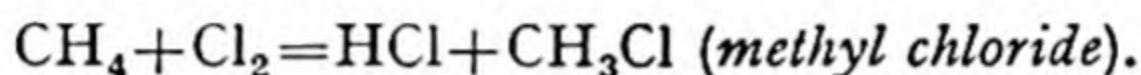
of absorbed light) leads to the formation of about a million molecules of hydrogen chloride.

An interesting fact is that the photochemical union of hydrogen and chlorine may not take place *immediately* on exposure to light, but may be preceded by a short *period of induction*. This represents the time taken by the activated chlorine to destroy impurities which act as negative catalysts upon the combination.

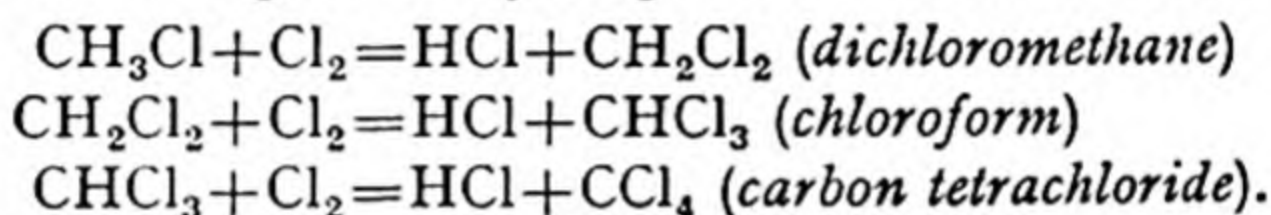
A mixture of chlorine and hydrogen, or chlorine and methane, will explode if ignited:



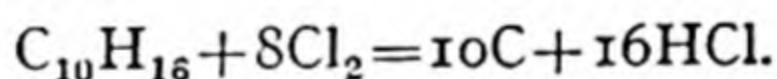
If chlorine and methane are mixed in diffused daylight, a different reaction occurs, a chlorine atom being substituted for a hydrogen atom in the methane molecule:



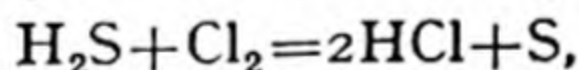
By further action of chlorine upon the product it is possible to replace the remaining three hydrogen atoms one after the other:



Chlorine will also extract hydrogen from many other hydrocarbons. Thus, if cotton wool soaked in warm turpentine ($\text{C}_{10}\text{H}_{16}$) is dropped into a jar of chlorine, hydrogen chloride and carbon are formed with a reddish, sooty flame:

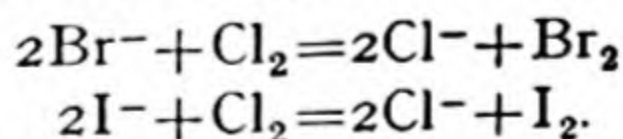


Chlorine liberates sulphur from moist hydrogen sulphide:

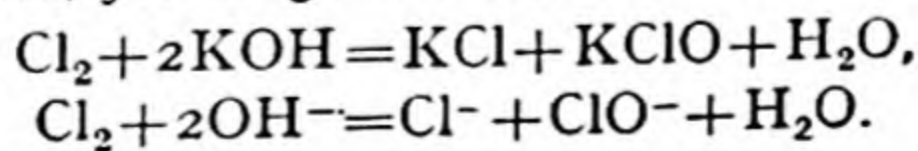


and combines directly with most metals to form chlorides. Phosphorus takes fire spontaneously in the gas, forming phosphorus tri- and penta-chlorides. With carbon monoxide, chlorine combines in sunlight to form the extremely poisonous gas *carbonyl chloride*, COCl_2 , otherwise known as *phosgene* ('light-produced') in reference to the conditions under which it is formed.

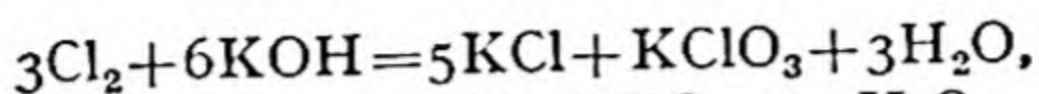
Chlorine liberates bromine from bromides and iodine from iodides:



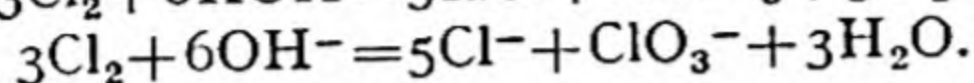
It dissolves in ice-cold aqueous solutions of potassium and sodium hydroxides, yielding a mixture of *chloride* and *hypochlorite*:



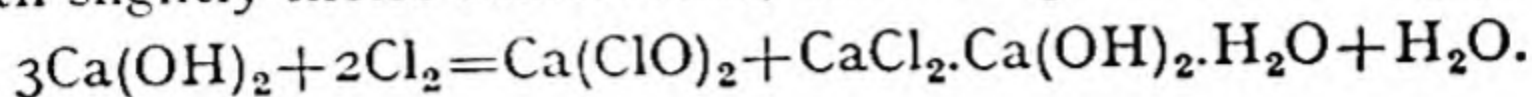
With hot aqueous alkali, a mixture of *chloride* and *chlorate* is formed:



or



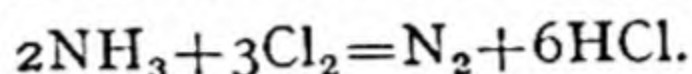
With slightly moist slaked lime, chlorine gives bleaching-powder:



(See p. 342.)

Chlorine will not combine directly with oxygen, but chlorine oxides may be prepared in other ways (p. 551).

When chlorine is mixed with gaseous ammonia a flash occurs and a mixture of hydrogen chloride and nitrogen is formed:



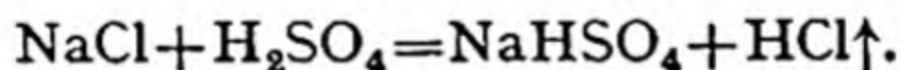
If the ammonia is in excess, the hydrogen chloride is converted into ammonium chloride. When chlorine is passed into aqueous ammonia a similar reaction occurs, though the explosive *nitrogen trichloride*, NCl_3 , may be formed if the passage of the gas is too prolonged.

The properties described above show chlorine to be a powerful oxidizing agent.

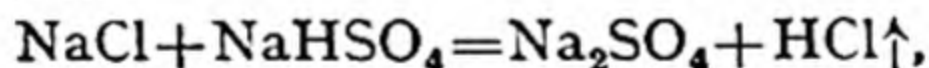
Uses. Chlorine is used for bleaching (p. 553), for sterilizing water, for detinning old tin-plate (p. 412), and for the preparation of many compounds. It is also used in the manufacture of plastics and synthetic rubber, and indirectly in the commercial hydrolysis of wood to dextrose (grape sugar).

HYDROGEN CHLORIDE, HCl

Preparation. In the laboratory, hydrogen chloride is prepared by warming rock-salt with concentrated sulphuric acid:



The further reaction:



takes place only at much higher temperatures.

The gas may be dried with concentrated sulphuric acid, and collected over mercury—or by air displacement, since it is somewhat denser than air.

If a steady stream of hydrogen chloride is required, it may be conveniently obtained by dropping concentrated sulphuric acid from a tap-funnel into concentrated hydrochloric acid.

Manufacture. Hydrogen chloride is manufactured mainly by the combustion of hydrogen in chlorine, the two by-products in the electrolytic manufacture of sodium hydroxide (p. 290).

Smaller quantities are obtained by an industrial adaptation of the laboratory method. Salt and chamber acid (p. 533) are mixed in the proportion of two molecules of NaCl to one molecule of H_2SO_4 , when sodium bisulphate is formed without the application of heat. The mixture of bisulphate with excess of salt is then raked on to the hearth of a reverberatory furnace and strongly heated. The hydrogen chloride evolved in both stages is passed up towers filled with acid-resisting cylindrical tiles over which a downward current of water flows. The solution leaving the towers has a density of 1.18–1.2, and contains about 36–38 per cent of hydrogen chloride; it is known as concentrated hydrochloric acid. The residue of sodium sulphate ('salt-cake') is used in glass-making, etc.

Hydrochloric acid prepared from synthetic hydrogen chloride is very pure. That obtained from salt is often yellow in colour owing to the presence in it of ferric chloride, and may also contain arsenic chloride if the chamber acid was prepared from pyrites (p. 532). The impure acid can be purified, but since it is already perfectly satisfactory for many industrial uses, and since the pure acid is more cheaply obtained synthetically, the crude salt-cake acid is usually sold as such. It is, in fact, a mere by-product of the manufacture of sodium sulphate.

Properties. Hydrogen chloride is a colourless, poisonous gas with a very pungent smell. It fumes strongly in moist air, for a reason discussed below. When cooled and compressed, it condenses to a colourless liquid boiling at -84° , and this can be frozen to a white crystalline solid (M.P. -111°). The solid, the liquid, and the dry gas are non-conductors of electricity, chemically inert, and without acid properties. Hydrogen chloride, when anhydrous, is

thus a covalent compound (p. 110) of the structure $\text{H} : \underset{\cdot\cdot}{\underset{\cdot\cdot}{\text{Cl}}} :$, the hydrogen and chlorine sharing a pair of electrons.

When, however, hydrogen chloride is dissolved in water, the covalent compound HCl becomes converted into the ions $(\text{H}_3\text{O})^+$ and Cl^- (p. 502). The solution, which is strongly acid, is known as *hydrochloric acid*—a name that, for the reasons just outlined, should not be used for hydrogen chloride; even 'hydrochloric acid gas' is a misnomer for the latter, since the gas is not an acid.

The solubility of hydrogen chloride in water is very great. One c.c. of water will dissolve 507 c.c. of the gas at 0° , and 448 c.c. at 18° . The solution saturated at the latter temperature contains about 42 per cent of its weight of HCl, while commercial 'concentrated hydrochloric acid,' as previously mentioned, contains about 38 per cent HCl and has a specific gravity of 1.19–1.20. When the saturated solution is distilled, it begins to boil at about 88° , the

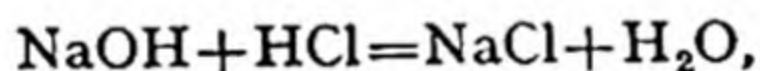
vapour given off being much richer in HCl than the solution itself. The residual liquid in the distilling-flask thus gradually becomes less concentrated, and this process continues, with steady rise of boiling-point, until the concentration falls to 20.24 per cent HCl. The liquid then gives a vapour of the same concentration as itself, and boils at a constant temperature (110° at 760 mm.).

On distillation of a more dilute solution, the vapour is at first richer in water than the solution, and the concentration of the residual liquid thus *rises*, finally reaching the value 20.24 per cent HCl as before. The liquid then distils unchanged. That this *constant-boiling* solution is a mixture and not a compound is shown by the fact that, at different external pressures, it has different concentrations of HCl.

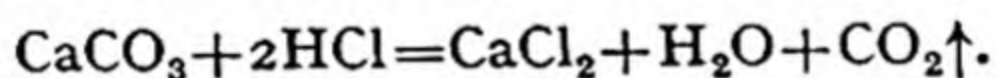
When hydrogen chloride comes into contact with moist air it forms a solution which has a lower vapour pressure than water at the same temperature. The solution therefore condenses in liquid droplets, and the gas 'fumes.'

Hydrochloric acid is a strong acid, readily dissolving many metals with evolution of hydrogen and production of the metallic *chloride*. It should be noted that when a metal forms two chlorides (iron, for example, forms ferrous chloride, FeCl_2 , and ferric chloride, FeCl_3), it yields the lower or *-ous* chloride with hydrochloric acid. On the other hand, such a metal with chlorine usually forms the higher or *-ic* chloride.

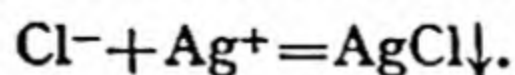
Hydrochloric acid will neutralize bases to form chlorides and water:



and will liberate carbon dioxide from carbonates:



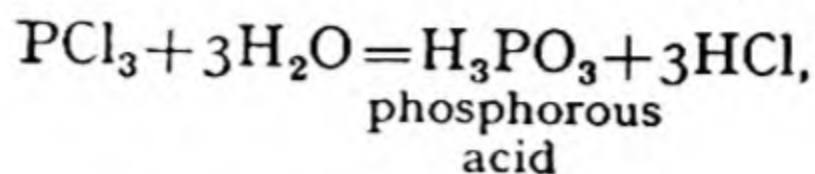
The *chlorides of metals* are salts and are almost all soluble in water; common exceptions are silver chloride, AgCl , mercurous chloride, Hg_2Cl_2 , and cuprous chloride, CuCl . (cf. Group I of the analysis tables). Lead chloride, PbCl_2 , is only slightly soluble in cold water, but dissolves much more readily in hot water. The presence of the chloride ion, Cl^- , in solution can be detected by adding silver nitrate solution, when a white, curdy precipitate of silver chloride is obtained. This precipitate darkens on exposure to light, and is soluble in ammonia solution but not in nitric acid:



Metallic chlorides when heated with manganese dioxide and concentrated sulphuric acid yield chlorine.

The *chlorides of non-metals* are typically covalent compounds

and may be regarded as derivatives of hydrogen chloride rather than of hydrochloric acid. Many of them are hydrolysed by water:



though there are exceptions, e.g. carbon tetrachloride, CCl_4 . None of them is a salt.

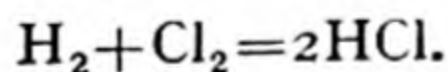
Composition of hydrogen chloride. In Fig. 98, the arm A of the tube has twice the capacity of the arm B. A is filled with hydrogen and B with chlorine. Tap T is opened to allow the gases to mix, and the apparatus is exposed to diffused daylight for about 48 hours. On opening tap W under mercury, no gas escapes and no mercury



FIG. 98. COMPOSITION OF HYDROGEN CHLORIDE

enters; hence the total volume of residual gases is the same as that of the original mixture. On opening tap X under water, water enters the apparatus and fills the whole of arm A. The residual gas in B can be shown to be hydrogen. The volume of the water entering the apparatus is the volume of the hydrogen chloride formed.

Therefore *one volume* of chlorine combines with *one volume* of hydrogen, forming *two volumes* of hydrogen chloride. Assuming AVOGADRO'S principle, and taking the formulae of hydrogen and chlorine to be H_2 and Cl_2 , respectively, this result may be written



Electrolysis of hydrochloric acid. If a direct current is passed between carbon electrodes in concentrated hydrochloric acid, hydrogen appears at the cathode and chlorine at the anode. Chlorine, however, is soluble in water and is adsorbed by carbon, hence the volume of gas at the anode is less than that at the cathode. By running the current for a considerable time before collecting the gases, the carbon anode and the solution can be saturated with chlorine. The volume of hydrogen collected at the cathode is then found to be roughly equal to the volume of chlorine collected at the anode; but the experiment is not very satisfactory.

Electrolysis of dilute hydrochloric acid yields hydrogen at the cathode and *oxygen* at the anode (see p. 39).

OXIDES AND OXYACIDS OF CHLORINE

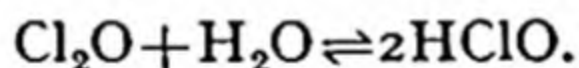
<i>Oxide</i>	<i>Formula</i>	<i>Acid</i>	<i>Formula</i>
Chlorine monoxide	Cl_2O	Hypochlorous	HClO
Chlorine dioxide	ClO_2	{ Chlorous Chloric	HClO_2 HClO_3
Chlorine 'trioxide'	Cl_2O_6	{ Chloric Perchloric	HClO_3 HClO_4
Chlorine heptoxide	Cl_2O_7	Perchloric	HClO_4

The names and formulae of the oxyacids, and the principal oxides, of chlorine are shown in the above table.

Chlorine monoxide, Cl_2O , is prepared by passing dry chlorine over dry, freshly precipitated mercuric oxide in a tube surrounded by ice-water:



Chlorine monoxide is a yellowish-red gas which can be condensed to a golden-brown liquid boiling at about 3° . It is an unstable, endothermic compound (ΔH , 17.9 kcal.) liable to explode on standing, or when brought into contact with organic matter. It dissolves in water, forming *hypochlorous acid*, HClO , of which it is the anhydride:

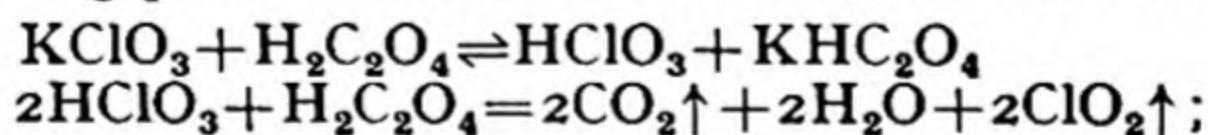


Chlorine dioxide, ClO_2 , a *dangerously explosive* gas, is produced in the following reactions:

- (a) by warming a solution of potassium chlorate made in ice-cold sulphuric acid to 35° :



- (b) by reducing potassium chlorate with oxalic acid at 60° :

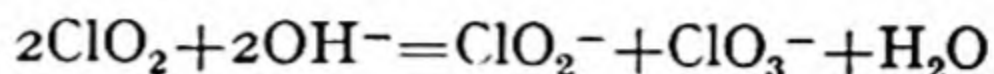


- (c) by passing chlorine over silver chlorate at 90° :



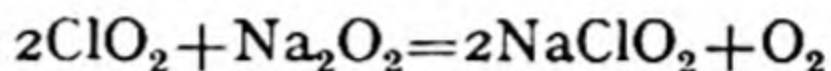
Of these methods only the last is relatively safe. Chlorine dioxide is easily separated from the gaseous products by freezing (M.P. -79°).

Chlorine dioxide is a yellow gas of unmistakable and penetrating odour. It can be condensed to an orange-red liquid boiling at $9-10^{\circ}$, and frozen to a red solid (M.P. -79°). It is very soluble in water, and dissolves in caustic alkali solution to give a mixture of *chlorite* and *chlorate*:



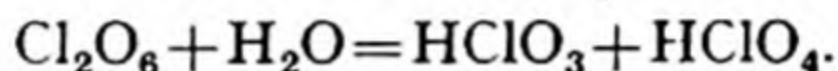
It is thus the mixed anhydride of chlorous and chloric acids.

A solution of pure chlorite is obtained by passing the dioxide into an aqueous solution of sodium peroxide:

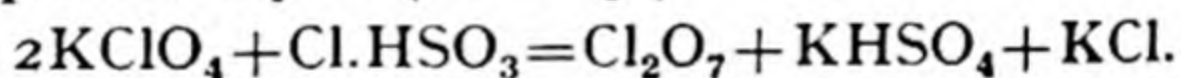


Chlorine dioxide explodes violently when heated, when brought into contact with phosphorus, dust, or organic matter, and when exposed to bright sunlight. It is an extremely energetic oxidizing agent.

Chlorine 'trioxide,' Cl_2O_6 , is an unstable liquid prepared by the action of ozone upon chlorine dioxide at 0° . It spontaneously decomposes into chlorine dioxide, chlorine, and oxygen. With water it yields a mixture of chloric and perchloric acids:



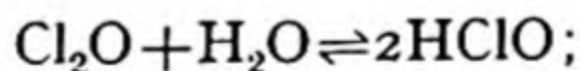
Chlorine heptoxide, Cl_2O_7 . A mixture of finely ground potassium perchlorate with chlorosulphonic acid Cl.HSO_3 (p. 523) is distilled under reduced pressure, when the heptoxide collects as a colourless, oily, and explosive liquid (B.P. 83°):



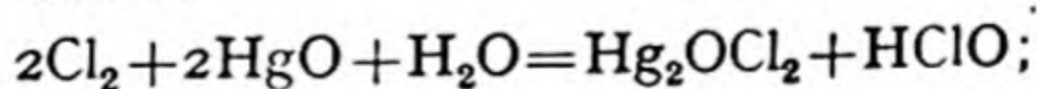
It is the anhydride of perchloric acid, which is quietly formed on dissolving it in water. Like chlorine dioxide, it is liable to explode violently.

Hypochlorous acid, HClO , has not been prepared anhydrous. Its aqueous solution can be obtained in several ways, e.g.:

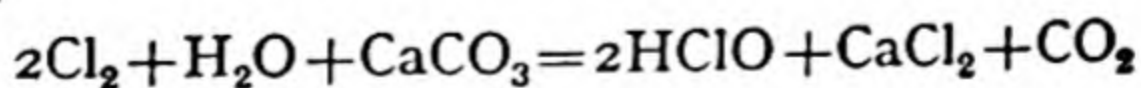
(a) by passing chlorine monoxide into water:



(b) by passing chlorine into a suspension of precipitated mercuric oxide in water:



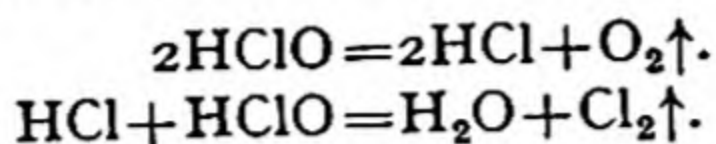
(c) by passing chlorine into a suspension of calcium carbonate in water:



The fact that the acid does not attack calcium carbonate is evidence of its weakness ($K \approx 10^{-8}$).

A solution of hypochlorous acid is pale yellow in colour, and smells

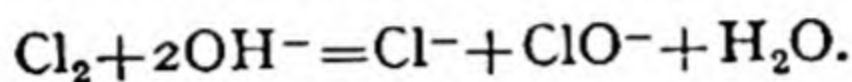
of bleaching-powder. It decomposes on standing, especially in the presence of sunlight, yielding mainly oxygen but a little chlorine:



On distilling the dilute aqueous solution under reduced pressure, hypochlorous acid, which is volatile, accumulates in the distillate, without appreciable loss by decomposition.

Hypochlorous acid is an energetic oxidizing agent, a characteristic which it shares with its salts, the hypochlorites.

Sodium hypochlorite, NaClO , may be prepared by passing chlorine into cold dilute sodium hydroxide solution:



Excess of chlorine should be avoided, since if the solution becomes acid the hypochlorite is soon converted into chlorate—a change also accelerated by rise of temperature.

Sodium hypochlorite is quite stable, and may be preserved for long periods, in aqueous solution, provided the solution remains alkaline in reaction: on the other hand, as mentioned above, hypochlorous acid is sufficiently stable to be distilled from its aqueous solution. It follows that chlorate cannot arise directly either from hypochlorite ion, ClO^- , alone, or from the acid alone. It is, in fact, produced only when a faint acidity allows both the acid, HClO , and the ion, ClO^- , to co-exist in the solution (see p. 296, equation (iii)).

A solution of sodium hypochlorite is obtained industrially by the above method, and also by the electrolysis of brine, the cathode and anode products (sodium hydroxide and chlorine) being allowed to mix and react. A similar solution of potassium hypochlorite, KClO , is commonly known as *eau de Javel*,* since it was first prepared at the Quai de Javel chemical works in Paris.

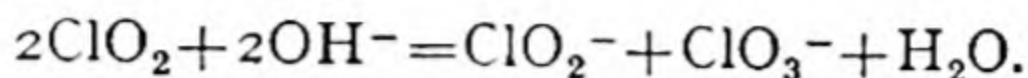
Calcium hypochlorite, $\text{Ca}(\text{ClO})_2$, is a constituent of bleaching-powder (p. 342).

The principal use of hypochlorites is in bleaching. When acted upon by a dilute acid (the 'carbonic acid' of the atmosphere is often sufficient), they yield hypochlorous acid, and this bleaches organic colouring-matters by a process of oxidation. Since the molecules of the coloured substance usually undergo a far-reaching disintegration, the bleaching is permanent (*contrast* the bleaching action of sulphur dioxide, p. 526). The bleaching effected by chlorine—which must be moist—is also ascribed to the hypochlorous acid formed by the reaction $\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HCl} + \text{HClO}$.

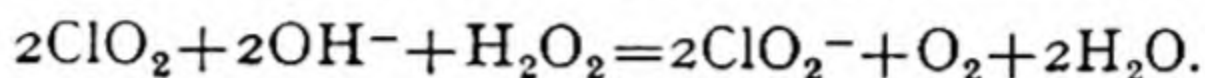
* The French Academy says *Javelle*; the great French lexicographer LAROUSSE says *Javel*. 'Javelles' is definitely incorrect.

Hypochlorites are good germicides and are widely used as such.

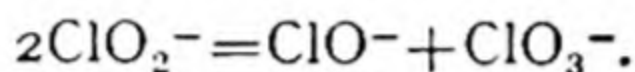
Chlorous acid, HClO_2 . It was mentioned on p. 552 that when chlorine dioxide is dissolved in aqueous alkali, a mixture of chlorite and chlorate is formed:



If, however, chlorine dioxide is passed into a solution containing alkali and hydrogen peroxide, only chlorites are formed:

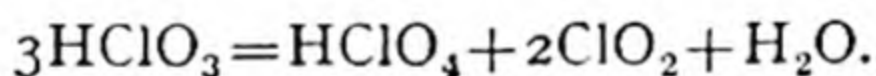


Chlorous acid may be obtained by carrying out this reaction with barium hydroxide as alkali, and precipitating the barium by addition of the required quantity of dilute sulphuric acid. After filtration, a colourless solution of chlorous acid is left. It rapidly decomposes, giving hypochlorous and chloric acids by disproportionation:



The *chlorites* are vigorous oxidizing and bleaching agents.

Chloric acid, HClO_3 , is prepared in aqueous solution by adding the theoretical quantity of dilute sulphuric acid to a solution of barium chlorate, $\text{Ba}(\text{ClO}_3)_2$. The precipitate of barium sulphate is filtered off, and the solution is concentrated by evaporation over sulphuric acid at reduced pressure until it contains about 40 per cent of chloric acid. Attempts at further concentration result in the decomposition of the acid into perchloric acid and chlorine dioxide:

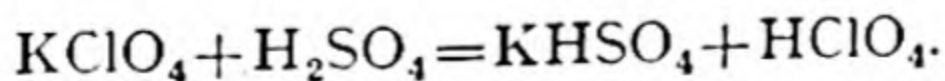


Like other oxyacids of chlorine, chloric acid is a strong oxidizing agent, readily inflaming organic material, and converting sulphur dioxide to sulphuric acid, hydrochloric acid to chlorine, and hydrogen sulphide to sulphur.

For *sodium chlorate*, see p. 296, and for *potassium chlorate*, see p. 306.

All chlorates are soluble in water, and their aqueous solution gives no precipitate with silver nitrate. They may be distinguished from most other oxidizing agents by the fact that, in acidified aqueous solution, they bleach indigo.

Perchloric acid, HClO_4 , is prepared by distilling (under reduced pressure) a mixture of potassium perchlorate and concentrated sulphuric acid:



It is a heavy, oily liquid which fumes in moist air and can be frozen to a colourless crystalline solid (M.P. -112°). With water it

combines violently to form hydrates, e.g. the crystalline monohydrate, $\text{HClO}_4 \cdot \text{H}_2\text{O}$. The pure acid is liable to explode on standing, or when warmed, and ignites wood, paper, and similar organic material. The dilute solution, however, is stable and possesses little oxidizing power. Perchloric acid is among the strongest acids known, and unlike many inorganic acids (e.g. nitric acid, p. 220) retains its strength in organic solvents such as alcohol. It is an interesting fact that the acids phosphoric, sulphuric, and perchloric, derived from the neighbouring elements phosphorus, sulphur, and chlorine, and all giving rise to an anion of the type $(\text{XO}_4)^{n-}$, show a steady increase of strength as the central atom becomes heavier and the charge on the anion becomes less. It is probably this diminution of charge which determines the decreasing extent to which covalent acid is formed.

A 50–60 per cent solution of perchloric acid is used in testing for potassium, since potassium perchlorate (p. 307) is only slightly soluble in water (cf. p. 309).

The *perchlorates* are isomorphous with the permanganates. They are considerably more stable than the chlorates.

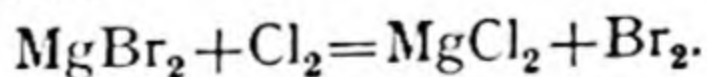
BROMINE, Br

Atomic number : 35. *Atomic weight* : 79.916. *Specific gravity* : 3.12.
Melting-point : -7° . *Boiling-point* : 59° .

History. Upon passing chlorine through the mother-liquor left after crystallizing salt from the salt-water of some marshes near Montpellier (France), BALARD (1826) noticed the formation of a brownish-yellow coloration. By evaporating the mother-liquor to dryness, and heating the residue with manganese dioxide and concentrated sulphuric acid, he was able to collect a dark reddish-brown liquid with a powerful and pungent smell. This liquid Balard called 'muride,' but when it was recognized to be a halogen, like fluorine, chlorine, and iodine, it was called bromine (Greek *brōmos*, a stench).

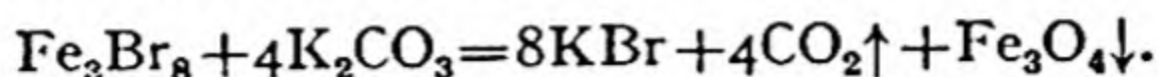
Occurrence. Bromine is a comparatively abundant element, though it does not occur in nature in the free state. It is contained, as sodium, potassium, and magnesium bromides (NaBr , KBr , and MgBr_2), in sea-water and in the water of certain salt springs, particularly in Ohio and Michigan, U.S.A. These bromides also occur in the great deposits of salts at and near Stassfurt, in the German provinces of Saxony and Hanover, and bromine is obtained from the latter source as well as from sea-water and the American brines. A little bromine was formerly extracted from the common seaweed (*Fucus vesiculosus*), the ashes of which contain about 0.7 per cent of the element. Small quantities of bromine occur naturally as silver bromide, and it is interesting to know that the celebrated Tyrian purple of antiquity, which was obtained from a species of mollusc, consists of dibromo-indigo.

Extraction. In the preparation of potassium chloride from carnallite (p. 305) at Stassfurt, the residual mother-liquor contains about 0.25 per cent of magnesium bromide. This liquor and the similar mother-liquor left after concentration of the American brines are both treated in the same way, which consists in exposing them to the action of chlorine:



The hot liquor trickles down a tall tower packed with broken bricks, earthenware balls, or glass balls, and meets an ascending current of chlorine and steam. The bromine vapour, together with a little chlorine, passes out of the top of the tower and is condensed in a water-cooled earthenware spiral. Any bromine escaping condensation is retained in secondary towers packed with moist iron filings, with which it reacts to form ferrous bromide, FeBr_2 , or, more probably, ferroso-ferric bromide, Fe_3Br_8 . The

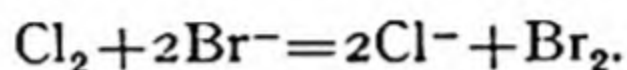
latter compound is used as a source of potassium bromide; it is dissolved in water and potassium carbonate is added, when double decomposition occurs and carbon dioxide is liberated:



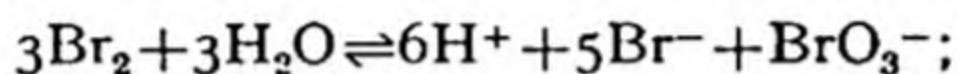
This method is also used in Palestine (Dead Sea), which supplies most of the bromine used in the British Commonwealth.

Various processes for obtaining bromine by electrolysis of the mother-liquors have been suggested, but are not generally used.

In America, bromine is extracted from sea-water, which contains about 0.007 per cent of the element in the form of the bromine ion, Br^- . On passing chlorine into sea-water, the bromine is liberated:



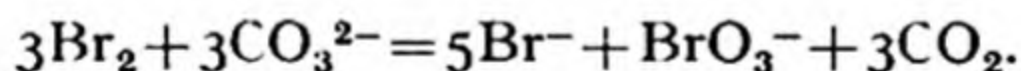
Sea-water is, however, slightly alkaline ($\text{pH} = 7.2$), hence much of the bromine is hydrolysed to bromate (or hypobromite) and bromide:



and since chlorine will not displace bromine from a bromate or hypobromite, considerable loss of bromine results.

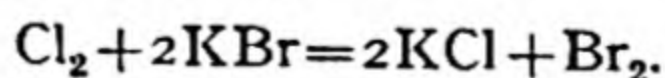
By adding sufficient sulphuric acid to the sea-water (about 1 lb. of acid to 4 tons of water), the pH can be lowered to 3.5, and at this value the hydrolysis of the bromine is negligible.

The acidified sea-water, after treatment with chlorine, trickles down towers up which a current of air passes. This blows out the bromine as vapour, and carries it on to further towers in which it is removed by sodium carbonate solution:



The solution of sodium bromide and bromate is treated with sulphuric acid to liberate the bromine, which vaporizes on heating and is condensed and collected.

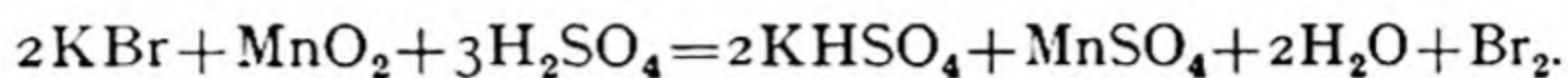
Purification. Common impurities in commercial bromine are chlorine, hydrogen bromide, iodine, and bromoform (CHBr_3); the last three are not always present and in any case their proportions are never very great. Chlorine is removed by adding powdered potassium bromide and distilling:



Bromine may be dried by shaking it with concentrated sulphuric acid.

Preparation. In the laboratory, bromine is conveniently prepared by distilling a mixture of potassium bromide and manganese dioxide with concentrated sulphuric acid. The bromine vapour is

condensed in a receiver over which a stream of cold water is allowed to flow:



Properties. Bromine is a dark reddish-brown liquid of density 3.12 gm. per c.c. It easily volatilizes, giving a poisonous dark red vapour with a very pungent and suffocating odour and with an irritating effect upon the eyes. The liquid itself, if it comes into contact with the flesh, produces severe burns; the best treatment for such wounds is to wash them with dilute sodium bicarbonate solution, then with alcohol, and finally with tannaflavine jelly or a freshly prepared solution of tannic acid.

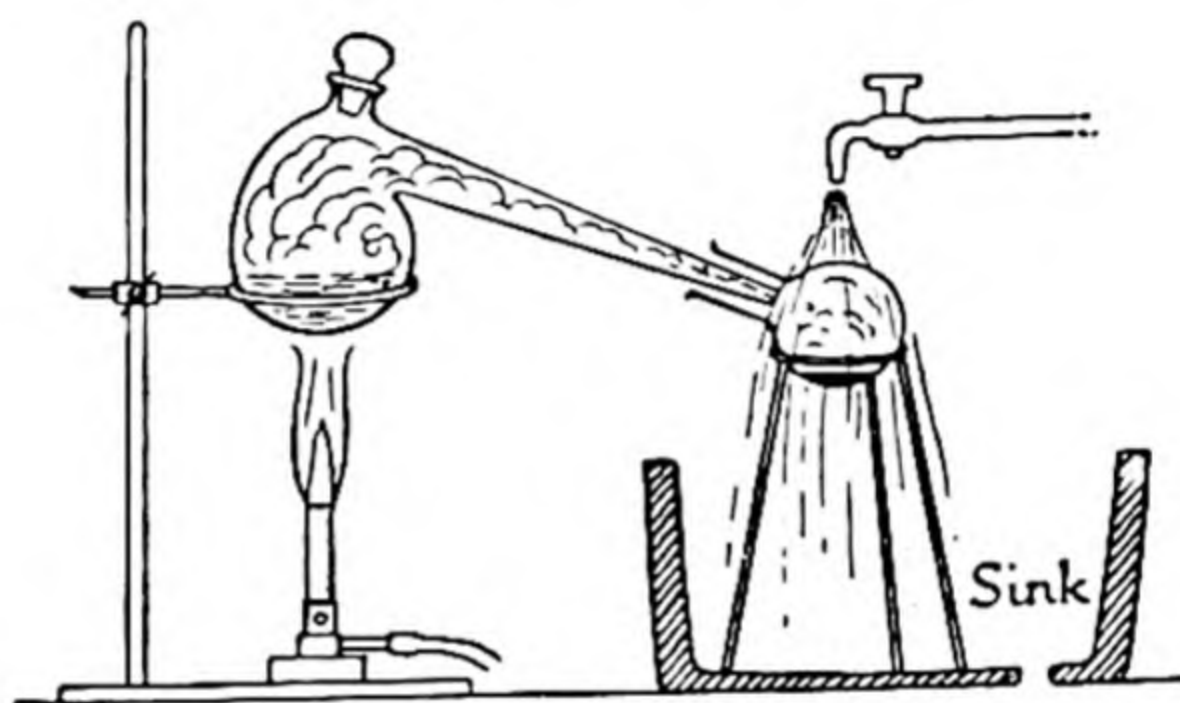
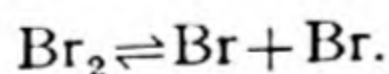


FIG. 99. LABORATORY PREPARATION OF BROMINE

Bromine freezes at -7.3° and boils at 59° . At temperatures only slightly above the boiling-point, the vapour has a density of rather more than 80. At about 200° the vapour density is normal (79.92), while at high temperatures it decreases owing to dissociation:



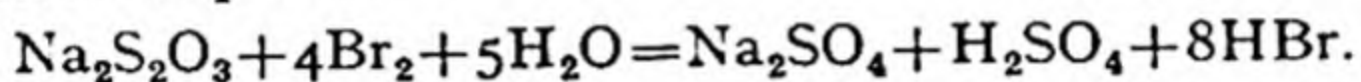
The extent of dissociation is, however, comparatively small, being only 4 per cent at $1,000^\circ$ and 18.3 per cent at $1,284^\circ$.

Bromine is slightly soluble in water, 3.98 gm. bromine dissolving in 100 gm. water at 0° and 3.46 gm. at 20° . On cooling the saturated solution, or on passing bromine vapour through a cooled tube moistened on the inside with water, hyacinth-red crystals of *bromine hydrate*, $\text{Br}_2 \cdot 8\text{H}_2\text{O}(?)$, are formed. When heated to 6.2° these crystals decompose into a solution of bromine in water and a solution of water in bromine. Bromine can be extracted from its

aqueous solution—which reacts acid owing to hydrolysis—by the addition of such solvents as chloroform, carbon tetrachloride, carbon disulphide, or benzene, in which the element readily dissolves. Bromine will also dissolve easily in potassium or sodium bromide solution, forming the complex ion Br_3^- . (Cf. *iodine*.)

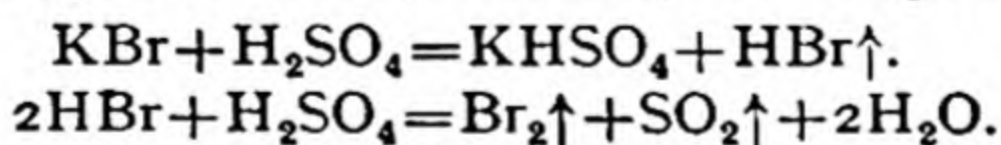
In its general chemical nature, bromine shows marked similarity to chlorine. Thus it will combine directly with hydrogen, on heating, forming *hydrogen bromide*, HBr , and with many metals, forming *bromides*. It will also combine very vigorously with yellow (less vigorously with red) phosphorus, yielding phosphorus tri- and penta-bromides, PBr_3 and PBr_5 . Like chlorine, too, moist bromine will bleach, though not so rapidly.

Bromine liberates iodine from potassium iodide solution, and may be estimated in this way, the iodine being determined with standard sodium thiosulphate (p. 537). Bromine with sodium thiosulphate gives sodium sulphate:

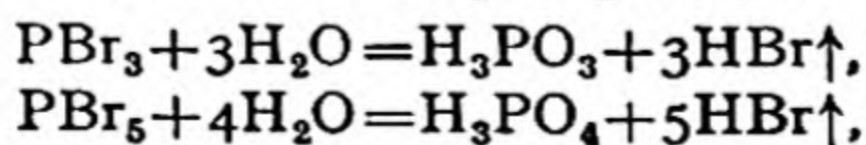


Uses. Bromine is used in medicine (as KBr), in photography (as AgBr), in the dye industry, and in the manufacture of drugs. Its principal use, however, is in the preparation of 'ethyl' petrol. This contains lead tetra-ethyl (p. 426) as an anti-knock. On explosion of the petrol-air mixture in the cylinders, the lead would soon foul the platinum points of the sparking-plugs unless steps were taken to remove it. Addition of ethylene dibromide, $\text{C}_2\text{H}_4\text{Br}_2$, to the petrol results in the formation of volatile lead bromide during the explosion, and this substance passes out with the exhaust gases. Several thousand tons of bromine are converted into ethylene dibromide every year for this purpose.

Hydrogen bromide, HBr . Hydrogen bromide may be prepared synthetically by passing a mixture of hydrogen and bromine vapour over a heated platinum or active carbon catalyst. It cannot be prepared pure by heating a bromide with concentrated sulphuric acid, since some of it is oxidized to bromine by the acid, which is itself reduced to sulphur dioxide. The product is therefore a mixture of hydrogen bromide, bromine, and sulphur dioxide:



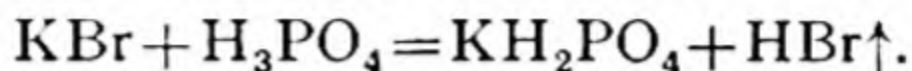
In the laboratory, hydrogen bromide is usually prepared by dropping bromine on to moist red phosphorus:



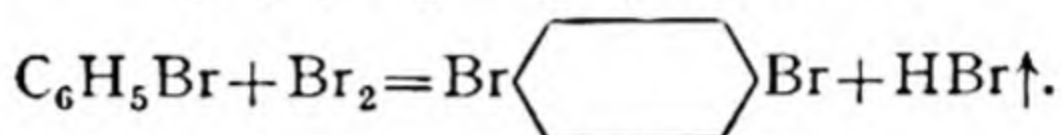
the bromides of phosphorus, presumed to be the first products,

being hydrolysed by the water. Any unchanged bromine vapour is removed by passing the gas through glass wool smeared with moist red phosphorus.

A more convenient method of preparing hydrogen bromide is to heat potassium bromide with syrupy phosphoric acid:

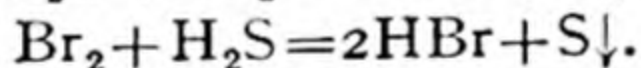
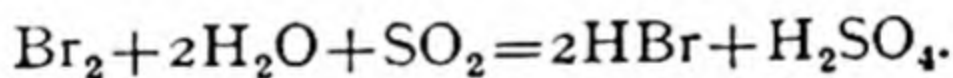


Hydrogen bromide is also set free when bromine acts upon benzene in the presence of aluminium, iron, or pyridine as catalyst; the other product is bromobenzene, $\text{C}_6\text{H}_5\text{Br}$, or—if the action is allowed to proceed further—para-dibromobenzene, $\text{C}_6\text{H}_4\text{Br}_2$:

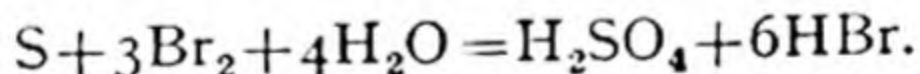


The gas prepared by any of these methods may be dried with calcium chloride and collected over mercury (or by air displacement, since it is much denser than air). If a solution is desired, the gas should be passed into water through one of the devices used to prevent 'sucking back.'

A solution may also be made by passing sulphur dioxide or hydrogen sulphide into bromine water, or bromine covered with bromine water:



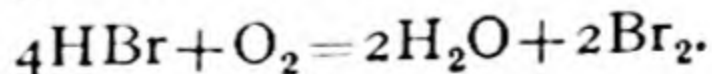
Another method is to dissolve sulphur in bromine and then hydrolyse the solution with cold water in the presence of excess of bromine:



On distilling, the sulphuric acid remains in the flask.

Properties. Hydrogen bromide is a dense, colourless gas closely similar to hydrogen chloride and hydrogen iodide. It has a pungent smell, and fumes in moist air. On cooling it condenses to a colourless liquid (B.P. -69°), which can be frozen to a white crystalline solid (M.P. -86°). It is readily soluble in water, with which it forms a constant-boiling mixture (B.P. 126°) containing 48 per cent of HBr.

The solution, known as hydrobromic acid, behaves as a strong acid; it is, however, not very stable and turns yellow in daylight on exposure to air, owing to the liberation of bromine:

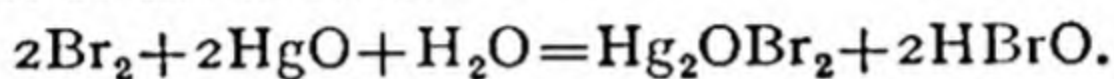


Bromides may be prepared by the usual methods. They are

isomorphous with the chlorides and are mostly soluble in water; silver, cuprous, and mercurous bromides are, however, insoluble, and lead bromide is sparingly soluble in cold water but more soluble in hot water. Silver bromide is used in photography (p. 327) as the light-sensitive substance. Potassium bromide (p. 305) is used in medicine as a sleeping-draught and sedative.

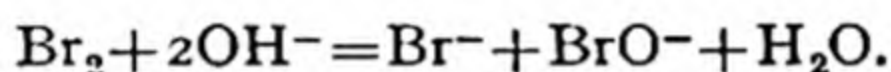
Oxides. Fluorine, chlorine, and especially iodine, all form oxides stable at normal temperatures. It is therefore remarkable that, though stable oxy-acids are derived from bromine, this halogen forms oxides that have only a fleeting existence even at low temperatures. By treating precipitated mercuric oxide with bromine vapour, evidence has been obtained for the initial formation of an oxide, Br_2O , but it decomposes into the elements so rapidly at 0° that little is known of its properties. An oxide even less stable results from treating bromine with ozone.

Oxyacids of bromine. A dilute solution of *hypobromous acid*, HBrO , can be prepared by shaking bromine water with precipitated mercuric oxide or silver oxide:



The solution is pale yellow in colour and very unstable. Like hypochlorous acid, it possesses oxidizing and bleaching powers.

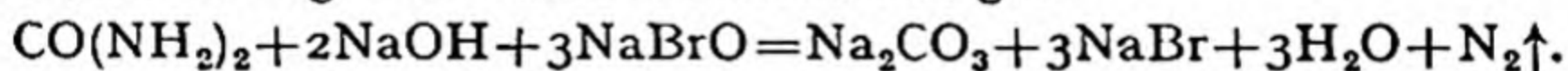
Hypobromites of the alkali metals may be prepared by the action of bromine upon cold dilute aqueous solutions of the metallic hydroxides:



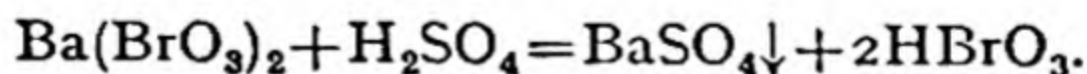
They cannot be isolated, and even in solution change rapidly into bromide and bromate:



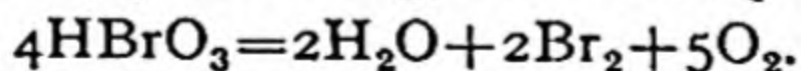
An alkaline solution of sodium hypobromite is used in estimating urea, the nitrogen of which it liberates as gas:



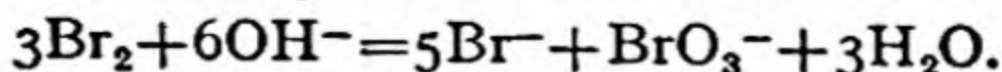
Bromic acid, HBrO_3 , can be obtained in concentrated solution—but not anhydrous—by addition of sulphuric acid to barium bromate solution and evaporation of the filtrate under reduced pressure:



Its solutions are strongly oxidizing, but decompose on heating:



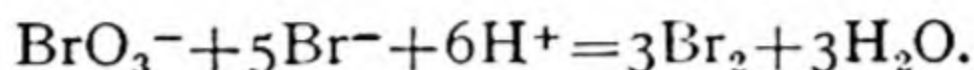
Potassium bromate can be prepared by dissolving bromine in concentrated potassium hydroxide solution:



Since potassium bromide is easily soluble in water, while potassium bromate is only sparingly soluble, separation may be effected without difficulty by fractional crystallization. Barium bromate may be prepared and isolated in a similar way, if hot concentrated barium hydroxide solution is substituted for the caustic potash solution.

On heating, most bromates decompose directly into bromides and oxygen: no *perbromates* are known.

An acidified solution of a bromate reacts gradually with a bromide as follows:



The reaction is strongly catalysed by addition of a few drops of aqueous ammonium molybdate.

IODINE, I

Atomic number: 53. Atomic weight: 126.91. Specific gravity: 4.9.
 Melting-point: 114° . Boiling-point: 184° .

History. Iodine was first discovered by a struggling French saltpetre manufacturer, BERNARD COURTOIS (1777-1838). One of the operations which Courtois was accustomed to carry out consisted in collecting seaweed along the coasts of Normandy and Brittany, burning it, and leaching out salts from the ash. The solution was then treated with sulphuric acid to destroy sulphides, sulphites, and thiosulphates. On a certain day in 1811, Courtois used an excess of concentrated acid, and was astonished at the formation of clouds of violet vapour, which on cooling yielded lustrous black crystals. He was a skilful chemist, and discovered many of the properties of the new substance, which he suspected to be an element; but he could not neglect his business long enough to carry out a thorough investigation. He therefore asked two other French chemists, CLÉMENT and DÉSORMES, to continue the work, an account of which they published in 1813. Further research on the element was carried out by DAVY and by GAY-LUSSAC, who showed it to be similar in its chemical properties to chlorine. The name *iodine* is derived from the Greek word meaning 'like a violet,' and refers to the violet colour of the vapour.

Occurrence. Free iodine probably does not occur in nature, but metallic *iodides* are widespread in small quantity, e.g. in sea-water. *Sodium iodate*, NaIO_3 , forms about 2 parts per thousand, by weight, of caliche (crude Chili saltpetre, p. 297); and organic compounds of iodine



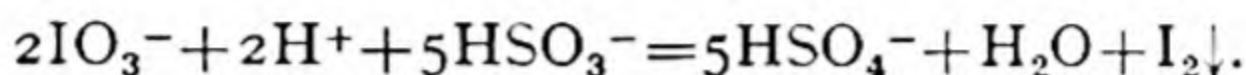
FIG. 100. SEALED TUBE CONTAINING IODINE PREPARED BY COURTOIS

(from Toraude, *Bernard Courtois et la découverte de l'Iode*)

NaIO_3 , forms about 2 parts per thousand, by weight, of caliche (crude Chili saltpetre, p. 297); and organic compounds of iodine

occur in the thyroid gland (cf. p. 566), in sponges, oysters and fish, and in seaweeds.

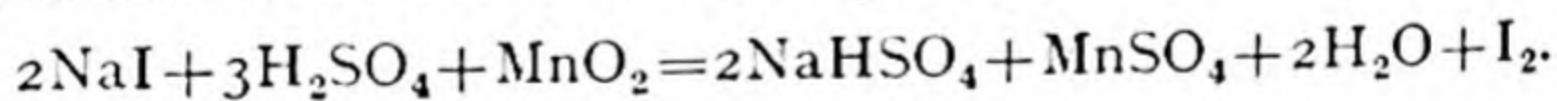
Extraction. The greater part of the world's supply of iodine is obtained from caliche. When the caliche is recrystallized, the sodium iodate is left in the mother-liquor. This is mixed with a solution of sodium bisulphite, in the proportion required by the equation:



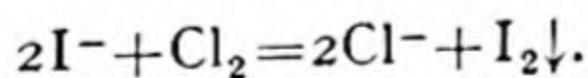
The precipitate of iodine is filtered off, washed, compressed into blocks, and purified by sublimation.

A secondary source of iodine, still employed to some extent, is seaweed; the kinds richest in iodine compounds are the kelps* (*Laminariaceae*) among the brown seaweeds (*Phaeophyceae*), and several species of deep-sea red seaweeds (*Rhodophyceae*). The seaweed is collected, and dried by exposure to the sun during hot weather. It is then piled into heaps and burned, when a residue of the chlorides, carbonates, sulphates, bromides, and iodides, etc., of sodium, potassium, and magnesium is obtained. A good deal of the iodine is lost during the combustion, and the kelp-burners acquire a spurious sunburn from the effect of its vapours.

The kelp-ash is extracted with water, and the solution, after decantation or filtration from insoluble matter such as charcoal, is concentrated. The chlorides, carbonates, and sulphates crystallize out, and the mother-liquor, containing sodium and potassium iodides with smaller quantities of the bromides, is mixed with manganese dioxide and concentrated sulphuric acid and distilled. Iodine comes off and is condensed in earthenware receivers. Bromine, evolved later, is condensed and collected separately:



In Russia, and in certain other countries where this process is still worked, the iodine is liberated by passing chlorine into the concentrated mother-liquor:

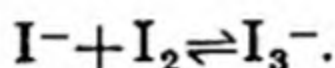


Commercial iodine frequently contains chlorine, bromine (iodine chloride, ICl , iodine bromide, IBr), and iodine cyanide, ICN . It can be freed from all these impurities by mixing it with a little powdered potassium iodide and gently heating the mixture. Iodine sublimes off, while the impurities are left as the non-volatile potassium salts, KCl , KBr , and KCN .

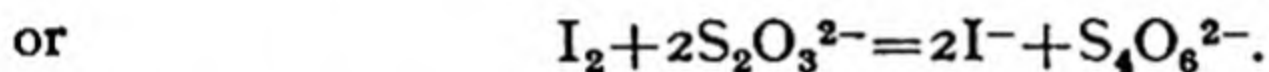
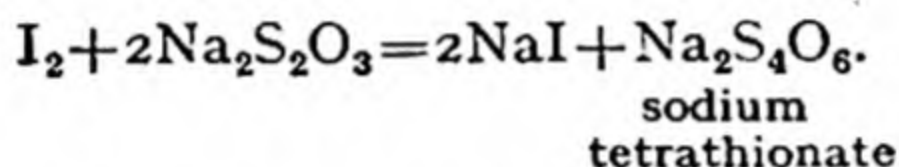
* *Kelp* primarily signifies the actual seaweed, but it is also used to denote the ash formed when seaweed is burned; this is better called *kelp-ash*.

Properties. Iodine forms black, shining, plate-like crystals of specific gravity 4.9; it melts at 114° and boils at 184° , but may be sublimed if heated to just below its melting-point. The density of the vapour at 400° is about 127 ($H=1$), showing that at this temperature the molecules are I_2 . With rise of temperature, dissociation occurs and the vapour density falls, becoming 63.5 at about $1,000^{\circ}$, when dissociation is complete: $I_2 \rightleftharpoons I + I$.

Iodine has a bitter taste, and a slight smell reminiscent of that of chlorine. It is only very sparingly soluble in water (0.29 gm./litre at 20°), but dissolves readily in potassium iodide solution owing to formation of the complex compound *potassium tri-iodide*, KI_3 :



Since the reaction is easily reversible, iodine dissolved in potassium iodide solution may be completely titrated with sodium thiosulphate as free iodine:

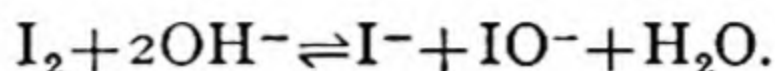


Iodine also dissolves in many organic solvents, e.g. alcohol, benzene, chloroform, ether, acetone, carbon disulphide, and carbon tetrachloride. The alcohol and ether solutions are brown, while the others are violet. It has been suggested that in the brown solutions the iodine has combined with the solvent.

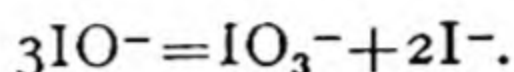
In its chemical properties, iodine is similar to the other halogens, but much less reactive. It combines directly with many metals to form *iodides*, often with incandescence (e.g. with sodium, potassium, moist aluminium powder). It also unites vigorously with phosphorus, forming PI_3 and P_2I_4 , and if heated with hydrogen gives rise to the equilibrium mixture $H_2 + I_2 \rightleftharpoons 2HI$ (hydrogen iodide). With starch solution, free iodine in the presence of iodide gives a characteristic deep blue colour, the cause of which is uncertain. This reaction affords a very sensitive test for iodine, the blue coloration being perceptible with as little as one part of iodine per million of water.

Iodine is a weak oxidizing agent, as evidenced by its reactions with (a) sodium thiosulphate (above), (b) hydrogen sulphide, which it oxidizes to sulphur (p. 521), and (c) arsenites, which it oxidizes to arsenates (p. 477). It may also act as a reducing agent, e.g. when heated with concentrated nitric acid, which it converts into oxides of nitrogen, being itself oxidized to *iodic acid* (p. 453).

Towards cold dilute aqueous alkali, iodine behaves in the same kind of way as the other halogens, forming an *iodide* and a *hypoiodite*:



Hypoiodites, however, are very unstable, passing quickly into *iodates* and *iodides* on warming, and less quickly even on standing in the cold:

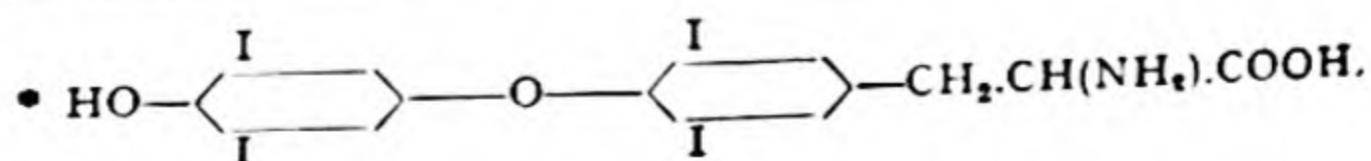
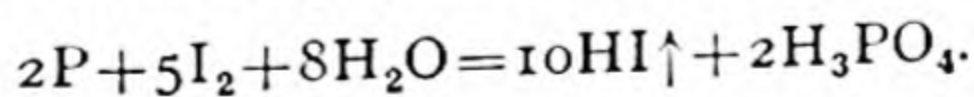


Uses. About 1,000 tons of iodine are produced annually, and this quantity could easily be increased if required. The greater portion is used in medicine, smaller amounts being consumed in the dye and photographic industries and in chemical research. Iodine is a remarkably powerful germicide, one part of iodine in 15,000 parts of water proving sufficient to kill even such resistant types as *Bacillus anthracis*, the anthrax bacillus. The popular antiseptic 'tincture of iodine' is a solution of which three common varieties are in use: *liquor iodi fortis* ('strong tincture of iodine'), prepared by dissolving iodine and potassium iodide in a little distilled water and diluting with 90 per cent alcohol to form a solution containing 10 gm. of iodine in 100 c.c.; *liquor iodi mitis* ('weak tincture of iodine'), a similar solution to the last but of one-quarter the concentration; and *liquor iodi simplex* ('simple—or "French"—tincture of iodine'), which is a solution containing 9 gm. of iodine dissolved in 100 c.c. of 95 per cent alcohol.

Iodine is secreted as its compound *thyroxine*, $\text{C}_{15}\text{H}_{11}\text{O}_4\text{NI}_4$,* by the thyroid gland in the front of the throat, and it has been shown that an adequate supply of thyroxine is essential to health. In many parts of the world, the soil contains too little iodine for ordinary foodstuffs to provide the necessary quantity, and in such regions iodine is sometimes added to the drinking water.

COMPOUNDS OF IODINE

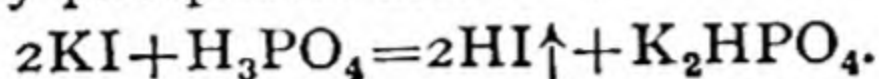
Hydrogen iodide, HI. The direct synthesis of hydrogen iodide, by passing a mixture of hydrogen and iodine vapour over a heated platinum catalyst, is unsatisfactory as a preparative method owing to its reversibility (p. 134). A more convenient method is to drop water on to a mixture of red phosphorus and iodine:



In practice, it is better to mix the red phosphorus and iodine with concentrated potassium iodide solution, warming the reaction flask if necessary. The evolution of hydrogen iodide is then more controllable.

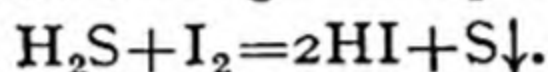
The gas is washed with a little water, and freed from any unchanged iodine vapour by passing it through a Drechsel bottle loosely packed with glass wool smeared with moist red phosphorus.

Hydrogen iodide may also be prepared by heating potassium iodide with syrupy phosphoric acid:



It can be dried with phosphorus pentoxide, and should be collected by air displacement (since it is over four times as dense as air, is very soluble in water, and attacks mercury).

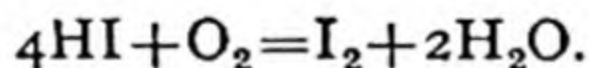
A solution of hydrogen iodide can be conveniently prepared by passing hydrogen sulphide through a suspension of iodine in water:



The sulphur is filtered off and the solution concentrated by evaporation until the constant-boiling mixture is formed; this boils at 127° and contains 58 per cent by weight of HI.

Hydrogen iodide is a colourless gas which boils at -36° and freezes at -51° . It has a pungent smell, and fumes in moist air (cf. p. 549). Like hydrogen chloride and bromide, it is extremely soluble in water, 1 c.c. of water dissolving about 420 c.c. of the gas at 0° . Unlike HCl and HBr, however, it is *endothermic* (heat of formation from solid iodine: 6.4 kcal.) and unstable; even a mild degree of heat will cause appreciable dissociation, while at 300° about 18 per cent of the gas has dissociated.

The aqueous solution of hydrogen iodide is known as *hydriodic acid*. It has strongly acid properties, but owing to its instability it also behaves as a powerful reducing agent. Thus mere exposure to the air causes liberation of iodine, the liquid becoming yellow and then brown:



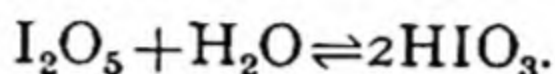
It will also reduce solutions of dichromates, permanganates, cupric salts, and ferric salts, and is widely employed in organic chemistry when drastic reduction is to be effected.

The *iodides* are mostly soluble in water, though those of mercury (*-ic* and *-ous*), silver, and copper (*-ous*) are insoluble, while lead iodide is sparingly soluble. Ferric and cupric iodides do not exist; addition of potassium iodide to copper sulphate solution, for example, yields a precipitate of cuprous iodide and iodine. Many iodides are coloured, e.g. mercuric iodide (red), silver iodide (pale yellow), lead iodide (bright yellow). *Potassium iodide*, KI, is described on p. 306.

When heated with concentrated sulphuric acid, it yields hydrogen iodide together with iodine, sulphur dioxide, sulphur, and hydrogen sulphide, the last four products resulting from the interaction of hydrogen iodide with the sulphuric acid.

Oxides of iodine. Iodine forms the oxides, I_2O_4 , I_4O_9 , and I_2O_5 , but of these only I_2O_5 is important.

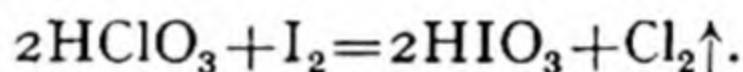
Iodine pentoxide, I_2O_5 , is a white, deliquescent, crystalline solid prepared by heating iodic acid (q.v.) to 196° . It dissolves in water, with which it re-forms iodic acid:



When iodine pentoxide is heated, it decomposes at 300° into iodine and oxygen. It is a vigorous oxidizing agent, and when dissolved in concentrated sulphuric acid will convert carbon monoxide into carbon dioxide—a property put to practical use in estimating carbon monoxide in gas mixtures.

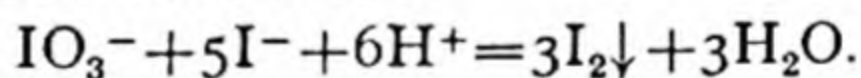
Hypoiodous acid, HIO , and the hypoiodites, are unstable compounds incapable of isolation.

Iodic acid, HIO_3 , is a colourless, deliquescent, crystalline solid prepared by heating iodine with concentrated nitric acid. It may also be prepared by warming iodine with aqueous chloric acid and evaporating the solution:



When heated to slightly above the boiling-point of water it is partially dehydrated, forming the compound $HI_3O_8 (=I_2O_5.HIO_3)$, and this in turn is converted into iodine pentoxide at 196° .

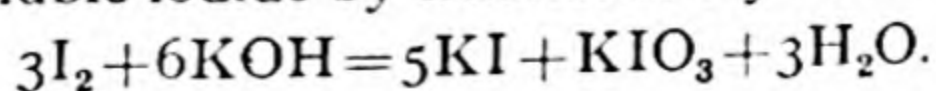
A solution of iodic acid bleaches litmus and liberates iodine from an acidified solution of an iodide:



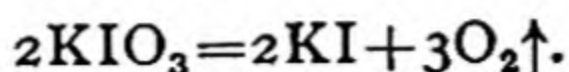
Mixtures of solid iodic acid with sulphur, phosphorus, or organic matter inflame when heated.

Potassium iodate, KIO_3 , is a white crystalline solid usually prepared by heating a mixture of water and potassium chlorate with iodine and a little nitric acid. The reaction $2KClO_3 + I_2 = 2KIO_3 + Cl_2$ proceeds only extremely slowly, but $KClO_3 + ICl = KIO_3 + Cl_2$, on the contrary, very rapidly: hence to start the reaction a small amount of chlorine is needed, and is usually produced by adding a few drops of nitric acid to the reaction mixture, when the above reaction with chloric acid, $HClO_3$, releases some chlorine.

It may also be obtained by dissolving iodine in hot concentrated caustic potash solution, and separating the sparingly soluble iodate from the very soluble iodide by fractional crystallization:

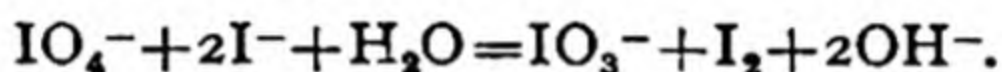


Like the chlorate and bromate, potassium iodate yields oxygen on heating, though less readily:



It can easily be obtained in a very pure state, and is therefore made up directly into standard solutions for standardizing sodium thiosulphate, iodides, etc., the reaction involved being that for which the equation was given above, viz. $\text{IO}_3^- + 5\text{I}^- + 6\text{H}^+ = 3\text{I}_2 + 3\text{H}_2\text{O}$.

Periodic acid, HIO_4 , is obtained by the electrolytic oxidation of a solution of iodic acid. On concentration, a white, deliquescent, crystalline solid of the formula H_5IO_6 separates out. This is para-periodic acid. By careful heating at 100° , under reduced pressure, para-periodic acid can be made to lose water and is converted into *meta*-periodic acid, HIO_4 . Most *periodates* are salts of para-periodic acid, but salts of still more complex periodic acids are known. On heating, they evolve oxygen and leave a residue of the iodate or, at a higher temperature, of the iodide. Periodates, unlike perchlorates, are powerful oxidizing agents, and are much used in estimations of organic compounds by oxidation. Even in alkaline solution, periodate oxidizes iodide to free iodine, itself being reduced to iodate. Only upon acidification does the iodate oxidize iodide (see equation above):



COMPARATIVE EXERCISES

1. Make an outline comparison table, suitable for reproduction in half an hour, showing the chief points of resemblance among the halogen elements. Commit this table to memory.
2. Compare and contrast the properties of chlorine and its compounds with those of bromine and its compounds.
3. Do the same for bromine and iodine.
4. Make a more detailed comparison table for the halogen acids, noting any peculiarities shown by HF and HI .
5. Tabulate the principal resemblances among (a) the oxides, and (b) the oxyacids, of the halogens.

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CHAPTER XXXI

TRANSITION METALS

AS EXPLAINED in Chapter VIII the first 'long series' (Series 4) of the periodic system, containing eighteen elements, opens with the metals K and Ca, falling quite appropriately under Na and Mg respectively in Series 3, and is concluded by the six elements Ga–Kr, each of which also finds an analogue in Series 3. Of the intervening metallic elements the set Ti–Mn conform moderately well in their *highest* valencies to the requirements of group analogies; but for their well-marked and often numerous lower valencies no such relationship is discernible. To the metals Fe, Co, and Ni Mendeléeff was unable to provide analogous elements in previous series, and he was compelled to place them in what he termed a 'transitional' Group VIII, which had in fact only an uncertain significance in the scheme of classification.

Our present knowledge of electronic atomic constitution (Chapter IX), however, now brings the series of metallic elements Ti–Cu into relationship, for in them the $3d$ atomic orbitals are progressively occupied up to a total of 10 electrons, which is the maximum number these orbitals can comprise. These elements are genuinely 'transitional' between the completion of the $4s$ orbitals (with 2 electrons) attained in Ca, and the filling of the $4p$ orbitals (with 6 electrons) begun in Ga ($3d^{10} 4s^2 4p$) and finally completed in Kr ($3d^{10} 4s^2 4p^6$). It is therefore profitable to treat these 'transition metals' (in the modern meaning) together as a separate group, and in this chapter we consider the metals Cr, Mn, Fe, Co, and Ni as successive examples of this treatment. Copper, in its *cupric* state Cu^{II} , is also within the transition group, and as will be seen on re-reading Chapter XXIII, pp. 318–321, its chemistry in this state is in many respects similar to that of Ni.

In addition to the characteristic properties of these transition metals mentioned in Chapter VIII, p. 82 and Chapter X, p. 110, the equality of their atomic radii is noteworthy:

	Cr	Mn	Fe	Co	Ni	Cu
$r_{\text{at.}} (\text{\AA})$	1.25	—	1.24	1.25	1.24	1.28.

The crystal structure of manganese is so exceptionally complicated that it is impossible to assign a definite atomic radius to this metal.

CHROMIUM, Cr

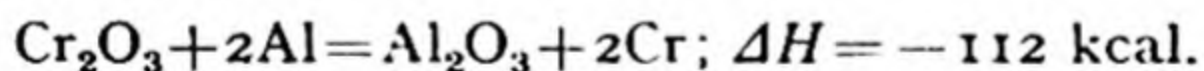
Atomic number: 24. *Atomic weight:* 52.01. *Specific gravity:* 7.1.
Melting-point: 1,850°. *Boiling-point:* 2,470°.

History. In 1762-6 LEHMANN described a new mineral called *crocoite* or *crocoisite*. In 1797 VAUQUELIN showed that it consisted of oxide of lead combined with the oxide of a new metal which he proposed to call *chromium*, on account of its characteristic property of forming coloured compounds (Greek *chrōma*, colour). Crude specimens of chromium were obtained by Vauquelin himself, and by DEVILLE (1857), but the pure metal was first prepared by MOISSAN in 1894.

Occurrence. Chromium does not occur free in nature. Its principal ore is *chrome iron ore* or *chromite*, the composition of which may be represented by the formula FeCr_2O_4 . X-ray examination shows that the substance is composed of the ions Fe^{2+} , Cr^{3+} , and O^{2-} , in the proportions of the formula. No compound ions can be detected.

Extraction. Much chromium is used in making chromium steel, and for this purpose the metal is extracted as an iron-chromium alloy, *ferrochrome*. Chromite is mixed with carbon and a flux, and heated strongly in a blast-furnace or electric furnace.

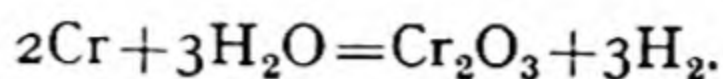
Commercially pure chromium is made by the GOLDSCHMIDT process. A mixture of chromium sesquioxide, Cr_2O_3 (prepared from chromite), and aluminium powder is ignited by a fuse of barium peroxide and aluminium powder, itself fired by a piece of burning magnesium ribbon. Once started the reaction takes place with evolution of much heat:



Pure chromium is also obtained electrolytically, as in *chromium plating*. The electrolyte is a solution of chromic acid with chromic sulphate, $\text{Cr}_2(\text{SO}_4)_3$, acidified with sulphuric acid.

Properties. Chromium is a hard white metal with a high melting-point (1,850°) and boiling-point (2,470°); its specific gravity is 7.1. It is remarkably stable in air at ordinary temperatures, and since it also takes a brilliant polish it is widely used in plating. When strongly heated in air or oxygen it can be made to take fire, burning brilliantly to form the *sesquioxide*, Cr_2O_3 . It dissolves easily in warm dilute hydrochloric and sulphuric acids, forming *chromous* (Cr^{2+}) salts, which, however, are readily oxidized to chromic (Cr^{3+}) compounds. Concentrated nitric acid renders chromium passive, but the dilute acid attacks it, forming *chromic* nitrate and oxides of

nitrogen. As with iron, steam is decomposed by chromium at a red heat:



Apart from its use in plating, chromium finds application in various important alloys. *Stainless steel* contains about 13–18 per cent of chromium. *Stellite* (p. 598) and other high-speed tool-steels contain chromium, tungsten, molybdenum, cobalt, and iron. *Nichrome*, the usual resistance wire in electric fires and heaters, has the composition Ni, 60; Fe, 25; Cr, 15 per cent.

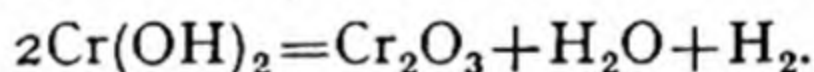
In its compounds chromium may show a valency of II, III, or VI. It has also been claimed that in a few compounds valencies of IV and V are shown, but this is not yet certain.

CHROMOUS COMPOUNDS

These contain the bivalent metal, and since they are extremely easily oxidized they are difficult to prepare and to keep. (p. 250).

Chromous oxide, CrO , is the black powder formed when chromium amalgam is treated with dilute nitric acid, or merely exposed to air.

Chromous hydroxide, $\text{Cr}(\text{OH})_2$, separates as a yellow precipitate when caustic alkali solution is added to a solution of a chromous salt. It dissolves in acids to give blue solutions of chromous salts, and on heating yields chromium sesquioxide, water, and hydrogen:

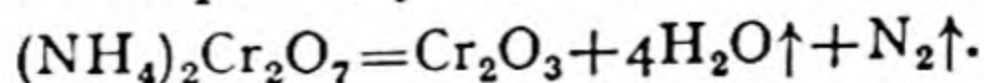


Chromous chloride, CrCl_2 , can be prepared as anhydrous silky white needles by passing a current of hydrogen chloride over the strongly heated metal. In solution—from which it crystallizes as the blue tetrahydrate, $\text{CrCl}_2 \cdot 4\text{H}_2\text{O}$ —it is formed when chromium is dissolved in dilute hydrochloric acid, and when a chromate or chromic salt is reduced with zinc and hydrochloric acid. Addition of concentrated sodium acetate to a solution of chromous chloride gives a red precipitate of *chromous acetate*, of empirical formula $\text{Cr}(\text{CH}_3\text{COO})_2$.

CHROMIC COMPOUNDS

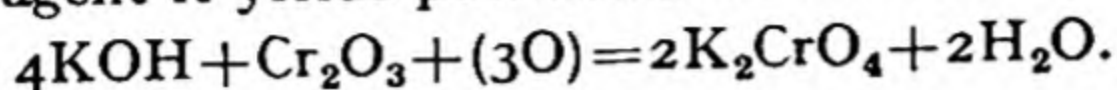
In chromic compounds, chromium is tervalent.

Chromic oxide, chromium sesquioxide, Cr_2O_3 , is produced when any of the other oxides is heated in the air. The simplest method of preparing it is to ignite ammonium dichromate; a vigorous reaction occurs and a powdery mass of the sesquioxide remains:

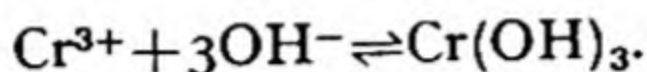


Chromium sesquioxide is a green solid used in industry as a

pigment. It is very difficult to reduce, insoluble in water, and difficultly soluble in acids. If fused with potassium hydroxide and an oxidizing agent it yields potassium chromate:



Chromic hydroxide, $\text{Cr}(\text{OH})_3$, is obtained as a greenish flocculent precipitate when a solution of sodium hydroxide, potassium hydroxide, or ammonia is added to a solution of a chromic salt:

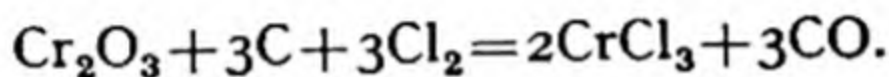


It is apt to carry some of the precipitating agent with it.

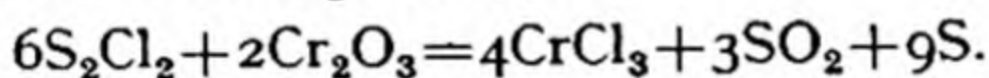
On boiling with excess of caustic alkali and hydrogen peroxide, chromic hydroxide is converted into chromate.

Chromic hydroxide is soluble in excess of caustic alkali to form a green colloidal solution, formerly thought to contain a chromite, e.g. NaCrO_2 . With dilute acids it yields chromic salts.

Chromic chloride, CrCl_3 , is made by heating chromium, or an intimate mixture of chromium sesquioxide and carbon, in a stream of chlorine:



A more convenient preparation is to pass sulphur monochloride vapour over the heated sesquioxide:



Anhydrous chromic chloride forms pink, scaly crystals which are practically insoluble in pure water, but dissolve readily in the presence of traces of chromous chloride (or a reducing agent, e.g. stannous chloride); the solution is green. *Chromic chloride hexahydrate*, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, exists in solution in three different forms: dark green, pale green, and violet. The first form loses only one-third of its chlorine on precipitation with silver nitrate, while the pale green form loses two-thirds, and the violet form the whole, of its chlorine. This is explained by the formation of complex cations:

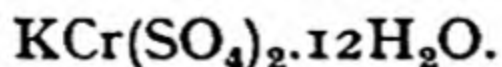
Dark green form: $[\text{CrCl}_2 \cdot 4\text{H}_2\text{O}]^+$

Pale green form: $[\text{CrCl} \cdot 5\text{H}_2\text{O}]^{2+}$

Violet form: $[\text{Cr} \cdot 6\text{H}_2\text{O}]^{3+}$

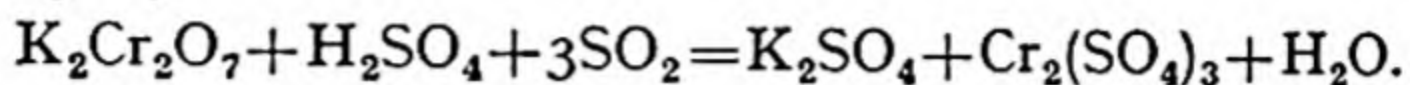
Chromic sulphate, $\text{Cr}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, is a violet crystalline substance made by digesting chromic hydroxide with cold concentrated sulphuric acid.

Chrome alum, potassium chromium sulphate,



This substance, a typical alum (p. 383), is prepared by acidifying

potassium dichromate solution with sulphuric acid and reducing with sulphur dioxide (or with alcohol, as in the preparation of acetaldehyde):

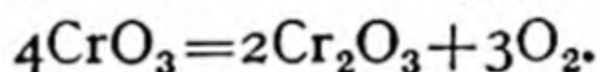


On concentrating the solution, the chrome alum separates out in violet octahedra. The solution should not be heated above 70° , for at higher temperatures a green solution is formed from which the alum will not crystallize. Chrome alum is used in the tanning of leather, which it renders more resistant to wear.

CHROMIC ACID, CHROMATES, AND DICHROMATES

Chromium trioxide, CrO_3 , is precipitated in the form of dark reddish-crimson needles when concentrated sulphuric acid is added to a cold saturated solution of potassium dichromate. The liquid, which becomes hot, is allowed to cool slowly, and the crystals of the trioxide are separated from the mother-liquor by decantation. They are washed with concentrated nitric acid and dried on a porous plate.

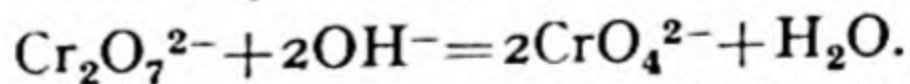
Chromium trioxide melts at 196° , and at a higher temperature decomposes into the sesquioxide and oxygen:



It is very soluble in water, with which it yields an acid solution believed to contain small quantities of *chromic acid*, H_2CrO_4 , and larger quantities of *dichromic acid*, $\text{H}_2\text{Cr}_2\text{O}_7$. Chromium trioxide is therefore alternatively known as *chromic anhydride*.

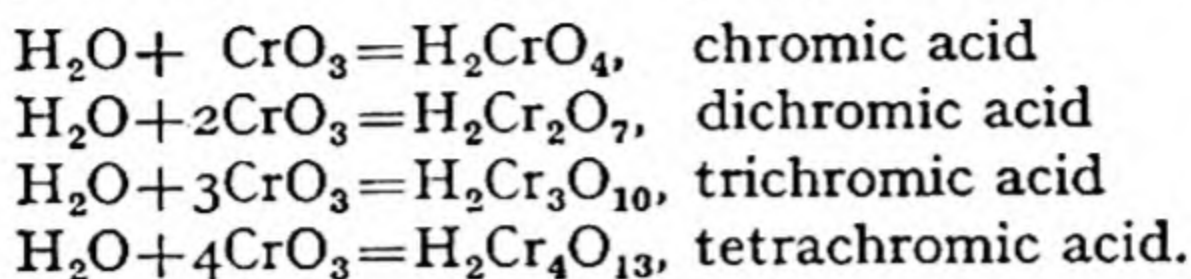
Chromium trioxide is a very powerful oxidizing agent, and may inflame such substances as filter-paper or alcohol. It oxidizes dilute alcohol to acetaldehyde and acetic acid.

Chromates. Chromic acid itself, H_2CrO_4 , has not yet been isolated, but its salts, the *chromates*, are well known. *Potassium chromate*, K_2CrO_4 , is prepared from potassium dichromate by addition of potassium hydroxide or carbonate.



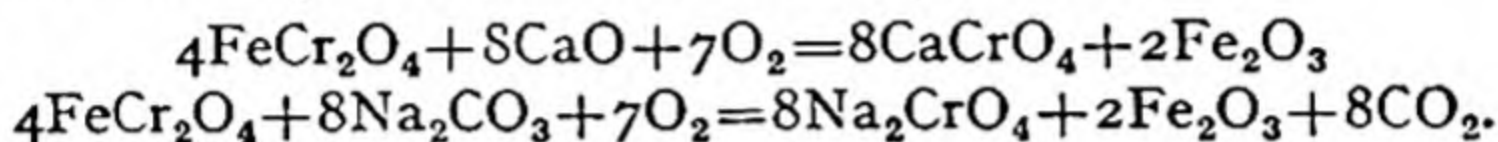
It is a yellow crystalline solid, used as an indicator in the titration of silver nitrate with a chloride, in neutral solution. *Barium chromate*, BaCrO_4 , *strontium chromate*, SrCrO_4 , and *lead chromate*, PbCrO_4 , are yellow insoluble substances; their formation in qualitative analysis is used as a test for the Ba^{2+} , Sr^{2+} , and Pb^{2+} ions. Lead chromate is used as a pigment (chrome yellow), while a basic lead chromate, $\text{PbCrO}_4 \cdot \text{PbO}$, is the conspicuous 'post office' red. *Silver chromate* is brick-red in colour, and the appearance of this colour marks the end-point in the silver nitrate-chloride titration when potassium chromate is used as indicator (see p. 326).

Dichromates. With water, chromium trioxide appears to be able to form a whole series of acids, mostly hypothetical:

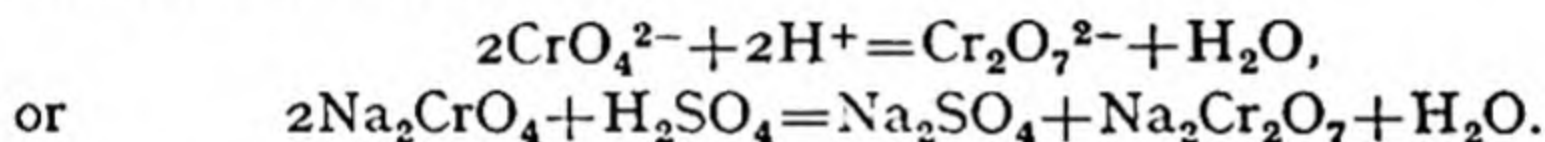


Salts of all these acids are known, but, apart from the chromates, the *dichromates* are the only ones of importance.

Sodium dichromate, $\text{Na}_2\text{Cr}_2\text{O}_7$, is manufactured by heating finely powdered chromite, FeCr_2O_4 , with quicklime and sodium carbonate in a reverberatory furnace with free exposure to air:

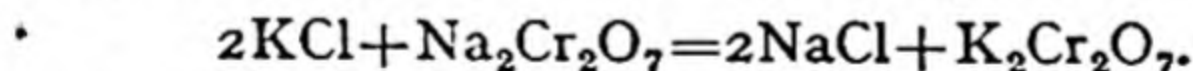


The melt is treated with hot concentrated sodium carbonate solution, to convert the calcium chromate into sodium chromate and to precipitate the calcium as carbonate. The solution of sodium chromate, after removal of insoluble matter, is concentrated, and then acidified with concentrated sulphuric acid; this converts the chromate into dichromate:

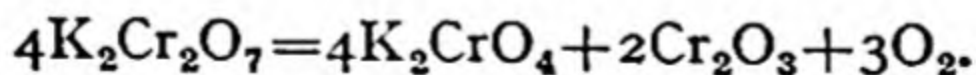


The sodium sulphate crystallizes out and is removed from the solution, which, after further concentration, deposits orange-red crystals of sodium dichromate dihydrate, $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$. This is much more soluble than potassium dichromate and is therefore preferred when a concentrated solution of a dichromate is required.

Potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$, is prepared by adding potassium chloride to a concentrated solution of sodium dichromate; it separates out in orange-red crystals, which, unlike those of the sodium salt, are anhydrous and non-deliquescent:

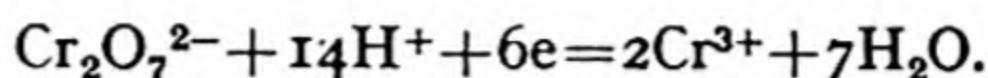


Potassium dichromate (like chromium compounds in general) is a poisonous substance; it melts at 399° , and decomposes into potassium chromate, chromium sesquioxide, and oxygen at high temperatures:



It is a powerful oxidizing agent, and in the presence of sulphuric acid quantitatively oxidizes ferrous iron to ferric iron, sulphurous acid to sulphuric acid, and potassium iodide to iodine. The chromium in the salt is reduced from the sexivalent to the trivalent

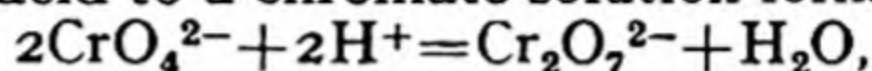
condition, and six electrons are absorbed by one G.F.W. of the dichromate:



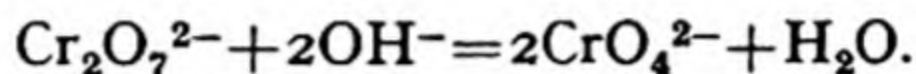
The equivalent of potassium dichromate is thus 49, i.e. one-sixth of its gram-formula weight (294).

In estimating ferrous iron, the dichromate solution is run into the acidified solution of the ferrous salt until the barium diphenylamine-sulphonate used as indicator turns violet-blue.

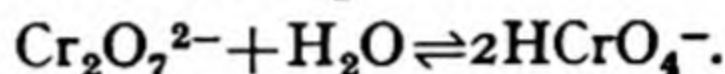
Addition of an acid to a chromate solution forms the dichromate:



and addition of an alkali to a dichromate solution forms the chromate:

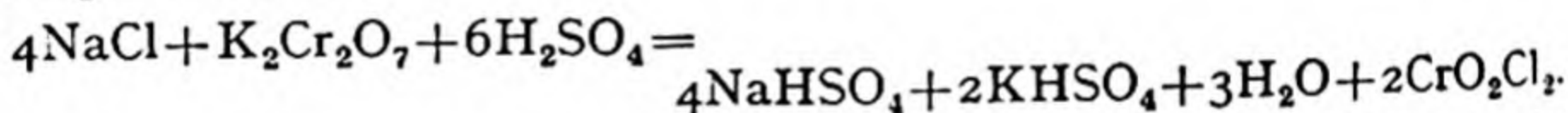


A dilute aqueous solution of potassium or sodium dichromate probably contains the ion HCrO_4^- :

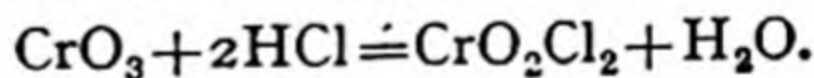


More concentrated solutions contain a greater proportion of $\text{Cr}_2\text{O}_7^{2-}$ ions.

Chromyl chloride, CrO_2Cl_2 , is prepared by distilling a dry mixture of potassium dichromate and sodium chloride with concentrated sulphuric acid:

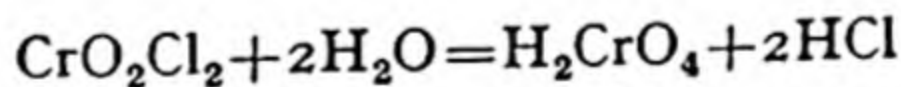


Alternatively concentrated sulphuric acid may be added to a cold solution of chromium trioxide in concentrated hydrochloric acid:



Chromyl chloride is denser than sulphuric acid, below which it forms a separate layer.

It is a heavy, dark red liquid of specific gravity 2, and boils at 117° . Water gradually hydrolyses it to 'chromic acid' and hydrochloric acid:



(cf. sulphuryl chloride: $\text{SO}_2\text{Cl}_2 + 2\text{H}_2\text{O} = \text{H}_2\text{SO}_4 + 2\text{HCl}$).

When chromyl chloride is poured into a saturated solution of potassium chloride, red crystals of *potassium chlorochromate*, $\text{K}.\text{CrO}_3.\text{Cl}$, are formed.

Chromyl bromide does not exist, a fact employed in the *detection of a chloride in presence of a bromide*. The substance is distilled dry, with potassium dichromate and concentrated sulphuric acid, and the fumes are dissolved in water. If a chloride was present, the solution will contain chromic acid, and this, after neutralization,

will give a yellow precipitate of lead chromate with a solution of lead nitrate or acetate.

Tests for Chromium.

1. Borax bead: green, in both oxidizing and reducing flames.
2. Fused with K_2CO_3 , Na_2CO_3 , and KNO_3 : yellow mass (containing a *chromate*).
3. Solutions containing the *chromic* ion give with
 - (a) ammonia solution: green gelatinous precipitate of chromic hydroxide, $Cr(OH)_3$;
 - (b) potassium hydroxide solution and hydrogen peroxide: yellow solution of chromate on warming.
4. *Chromates* and *dichromates* give with
 - (a) hydrogen peroxide and dilute sulphuric acid: deep blue liquid, from which the blue compound ('perchromic acid,' CrO_5) can be extracted with ether;
 - (b) barium chloride: yellow precipitate of barium chromate, $BaCrO_4$, insoluble in acetic acid, soluble in hydrochloric acid;
 - (c) silver nitrate: brick-red precipitate of silver chromate, Ag_2CrO_4 , insoluble in acetic acid, soluble in nitric acid and in ammonia.

MANGANESE, Mn

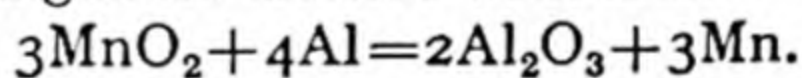
Atomic number: 25. *Atomic weight:* 54.94. *Specific gravity:* 7.06.
Melting-point: 1,245°. *Boiling-point:* 2,095°.

History. The black mineral form of manganese dioxide, MnO_2 , has been used for perhaps two thousand years in the fusion of glass, as a means of neutralizing the green colour imparted to glass by traces of iron. This accounts for the name of the mineral, *pyrolusite*, which comes from the Greek *pyr*, fire, and *lousis*, washing. Metallic manganese was first prepared in 1774 by GAHN, who reduced pyrolusite by heating it with carbon.

Occurrence. Manganese ores—chiefly the oxides *pyrolusite*, MnO_2 , and *braunite*, Mn_2O_3 , though the sulphide, *manganese blende*, MnS , is of some importance—are widely distributed and fairly abundant. The chief deposits are found in India, Georgia (U.S.S.R.), Brazil, United States, Ghana, Italy, and Spain.

Extraction. Though manganese is extensively used as an ingredient of special steels, it is not isolated as the pure element for this purpose. Instead a mixture of iron oxide and manganese dioxide is reduced with anthracite in the blast furnace to give the alloy *ferromanganese*, rich in manganese. This is then fused with ordinary steel in the requisite proportion.

Metallic manganese is best prepared by the GOLDSCHMIDT method, i.e. reduction of manganese dioxide with aluminium powder:



The crude metal so obtained can be purified by distillation under low pressure (1–2 mm.).

Properties. Manganese is a fairly hard white metal, stable in dry air. It slowly attacks water, even in the cold, forming manganous hydroxide, Mn(OH)_2 , with evolution of hydrogen, and is readily soluble in dilute acids, yielding solutions of pale pink manganous salts.

Its most remarkable property—which it shares with chromium—is a wide variation in valency; it shows, in fact, all valencies from II to VII inclusive, except V. The principal oxides are:

Manganous oxide, MnO . Strongly basic. Forms manganous salts.

Mangano-manganic oxide, Mn_3O_4 . 'Mixed' oxide.

Manganic oxide, Mn_2O_3 . Basic. Forms manganic salts.

Manganese dioxide, MnO_2 . Acidic dioxide.

Manganese heptoxide, Mn_2O_7 . Strongly acidic. Forms permanganates.

The ordinary manganese salts of the laboratory are *manganous*, in which the metal is bivalent.

Manganous oxide, MnO , can be prepared by reducing manganese dioxide in a current of hydrogen.

Manganous hydroxide, $\text{Mn}(\text{OH})_2$, is formed as a white precipitate on the addition of sodium hydroxide to a solution of a manganous salt. On exposure to air, it turns brown, owing to oxidation to hydrated manganese dioxide. Both manganous oxide and manganous hydroxide dissolve in dilute acids to form *manganous* salts.

Manganic oxide, Mn_2O_3 , occurs naturally as the mineral braunite, and may be prepared by heating manganese dioxide to about 800° or by drawing a current of air through a solution containing manganous ions, ammonium chloride, and ammonia. From it, the unstable manganic salts can be obtained by the action of concentrated acids.

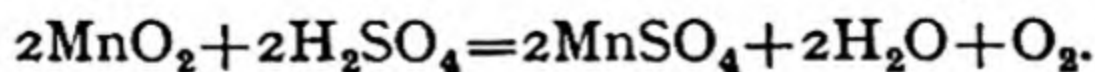
Manganese dioxide, MnO_2 , is the familiar black substance used in the laboratory for the preparation of chlorine from concentrated hydrochloric acid, and as a catalyst on the thermal decomposition of potassium chlorate. It can be prepared by the oxidation of a manganous salt, or the reduction of a permanganate, in alkaline solution; but the occasion seldom arises. On strong heating, it yields manganic oxide and oxygen at about 800° ; at higher temperatures the manganic oxide splits up into *trimanganese tetroxide*, Mn_3O_4 , and further oxygen.

MANGANOUS SALTS

Manganous salts are typically pale pink—almost colourless—and many of them are isomorphous with ferrous salts. Aqueous solutions of manganous salts are neutral in reaction.

Manganous chloride, MnCl_2 , may be made by dissolving manganese, manganous oxide, or manganous carbonate in dilute hydrochloric acid, and concentrating the solution by evaporation. On cooling, pink crystals of the tetrahydrate, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, separate out. The anhydrous salt may be obtained by heating the tetrahydrate, preferably in a current of hydrogen chloride.

Manganous sulphate, MnSO_4 , can be prepared in a similar way to the chloride, substituting dilute sulphuric acid for dilute hydrochloric acid. It is, however, commonly made by heating manganese dioxide with concentrated sulphuric acid and extracting the product with water:

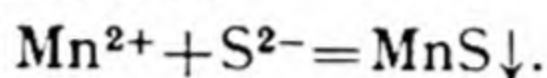


From aqueous solution it crystallizes (a) *below* 8° as the heptahydrate, isomorphous with 'green vitriol,' $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, and (b)

above 8° as the pentahydrate, isomorphous with 'blue vitriol,' $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

Manganous carbonate, MnCO_3 , is obtained as a white precipitate on addition of sodium bicarbonate to a solution of a manganous salt, a current of carbon dioxide being passed through the solution at the same time. Addition of sodium carbonate solution to a solution of a manganous salt gives a precipitate of manganous carbonate and manganous hydroxide; this rapidly goes brown on exposure to air, owing to oxidation. Manganous carbonate will slowly dissolve in water containing carbon dioxide, forming the bicarbonate $\text{Mn}(\text{HCO}_3)_2$.

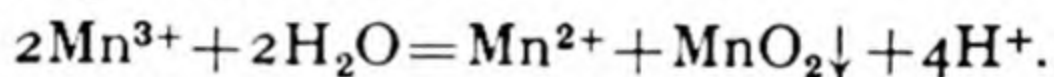
Manganous sulphide, MnS , is precipitated as a buff-coloured solid when ammonium sulphide is added (as in qualitative analysis) to a solution of a manganous salt:



It is soluble in acetic acid (*contrast* to zinc sulphide).

MANGANIC SALTS

Manganic salts are unstable in aqueous solution, since manganic ions, Mn^{3+} , readily attack water:



They are strong oxidizing agents.

Manganic chloride, MnCl_3 , is formed—together, probably, with some manganese tetrachloride, MnCl_4 —when manganese dioxide is dissolved in cold concentrated hydrochloric acid. It may be extracted from this solution with ether, and has been obtained as a black, unstable solid. With potassium chloride it forms the deep red complex salt *potassium manganichloride*, $\text{K}_2\text{MnCl}_5 \cdot \text{H}_2\text{O}$.

Manganic sulphate, $\text{Mn}_2(\text{SO}_4)_3$, is a deliquescent green crystalline solid made by the action of concentrated sulphuric acid on manganic oxide, Mn_2O_3 , or manganic acetate, $(\text{CH}_3\text{COO})_3\text{Mn}$. With ammonium sulphate and sulphates of the alkali metals, it forms red alums, e.g. $\text{KMn}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. These are isomorphous with other alums (p. 383).

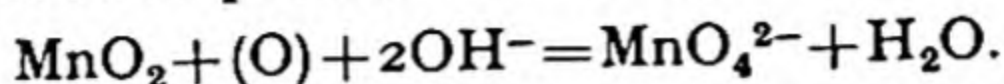
MANGANATES AND PERMANGANATES

Compounds in which manganese is sexivalent and septivalent are represented by the *manganates* and *permanganates* respectively.

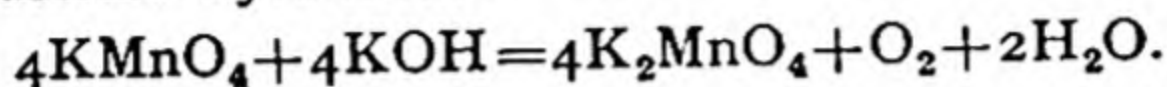
Manganates. Manganates are salts of manganic acid, H_2MnO_4 , which is the acid corresponding to an unknown oxide, MnO_3 . They are isomorphous with the chromates, selenates, and sulphates, are bright green in colour, and give the ion MnO_4^{2-} .

Potassium manganate, K_2MnO_4 , is made by fusing potassium hydroxide with manganese dioxide in the presence of an oxidizing

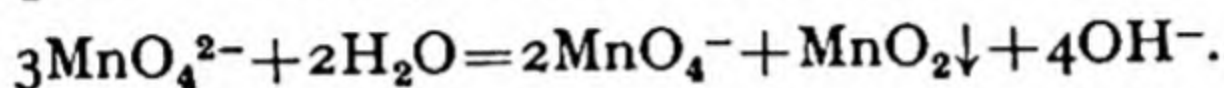
agent: even the air will serve, but it is customary to employ a more vigorous agent such as potassium nitrate or sodium peroxide:



The mass is extracted with water and the solution concentrated until it will deposit crystals on cooling. A simpler method of preparation is to digest potassium permanganate with concentrated aqueous potassium hydroxide:



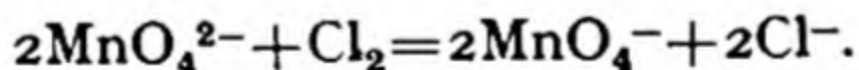
Potassium manganate—like the sodium salt, which it closely resembles in appearance, properties, and method of preparation—is stable in solution only in the presence of free alkali, i.e. in solutions in which the pH value is greater than 7. If the pH value is lowered, the solution changes to the purple colour of the permanganate, and a precipitate of manganese dioxide appears:



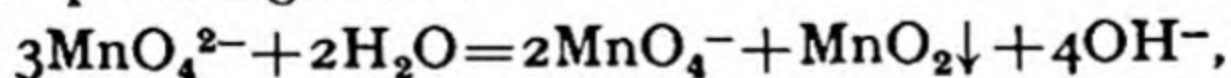
The formation of the characteristic green manganate on fusing a manganese compound with caustic alkali and an oxidizing agent is used as a test for the element.

Permanganates. Permanganates are salts of permanganic acid, HMnO_4 , the acid corresponding to manganese heptoxide, Mn_2O_7 . It is worth noticing that the manganates and permanganates are derivable from different oxides (viz. MnO_3 and Mn_2O_7), unlike the chromates and dichromates, which are both derived from chromium trioxide, CrO_3 .

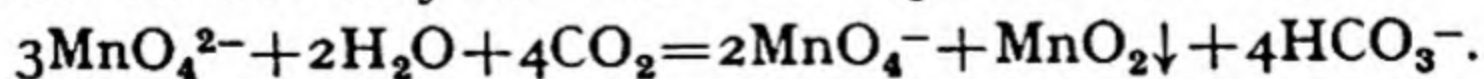
Potassium permanganate, KMnO_4 , was formerly known as the 'chemical chameleon' on account of its colourful reactions. It is prepared by fusing potassium hydroxide with manganese dioxide and an oxidizing agent (as for potassium manganate, above), extracting the mass with water, and oxidizing the manganate to permanganate either with chlorine or electrolytically:



Mere dilution of the manganate solution is sufficient to effect the formation of permanganate:



or carbon dioxide may be blown through the solution:

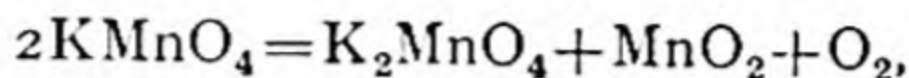


These methods are, however, less efficient than the former, since they involve a loss of one-third of the manganate as manganese dioxide.

Potassium permanganate forms dark purplish-black crystals isomorphous with potassium perchlorate. It was formerly believed to

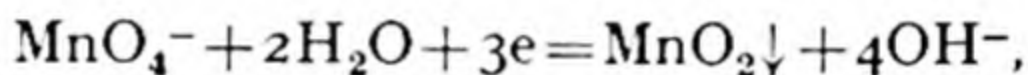
have the constitution $K_2Mn_2O_8$, but cryoscopic measurements indicate that it dissociates into 2 ions (K^+ and MnO_4^-), not 3 (K^+ , K^+ , and $Mn_2O_8^{2-}$), which it would presumably give if it were $K_2Mn_2O_8$.

Potassium permanganate is moderately soluble in water (2.83 gm. at 0° , and 6.38 gm. at 20° , per 100 gm. of water), in which it dissolves to give an intensely purple solution. On heating, it decomposes, apparently in a complex manner; the equation commonly given:

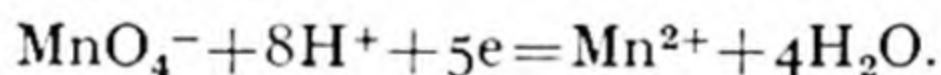


is only partially correct, though all three of these products are 'among those present.' It is an extremely powerful oxidizing agent, both in the solid state and in solution. A mixture of it with phosphorus will explode violently, while with glycerol it forms a mixture that inflames—often explosively—on warming. *Care should be taken never to heat it with concentrated sulphuric acid; the consequences of doing so have often been disastrous.*

In aqueous solution, potassium permanganate behaves as an oxidizing agent in two different ways, according as the solution is (a) neutral or alkaline, or (b) acid. In neutral or alkaline solution, the oxidizing reaction is:



while in acid solution it is:

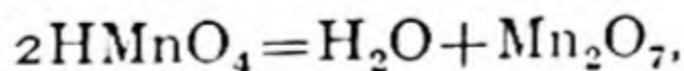


Hence, when potassium permanganate is being used in volumetric analysis, its equivalent is either 158 (G.F.W.) divided by 3, i.e.

52.7 (neutral or alkaline solution), or $\frac{158}{5}$, i.e. 31.6 (acid solution).

Potassium permanganate will oxidize ferrous salts to ferric salts, hydrochloric acid to chlorine, nitrites to nitrates, sulphites to sulphates, and many organic compounds to carbon dioxide and water. Its great power of oxidation is doubtless the explanation of its efficacy as a germicide.

If potassium permanganate is added to *ice-cold* concentrated (100 per cent) sulphuric acid, dark oily drops of *manganese heptoxide*, Mn_2O_7 , separate out. This substance, the anhydride of permanganic acid:



is a powerful oxidizing agent and is liable to explode. It dissolves in water to give a violet solution of permanganic acid.

Sodium permanganate, $NaMnO_4$, is a very soluble substance which gives a solution of the same colour as the potassium salt; the colour

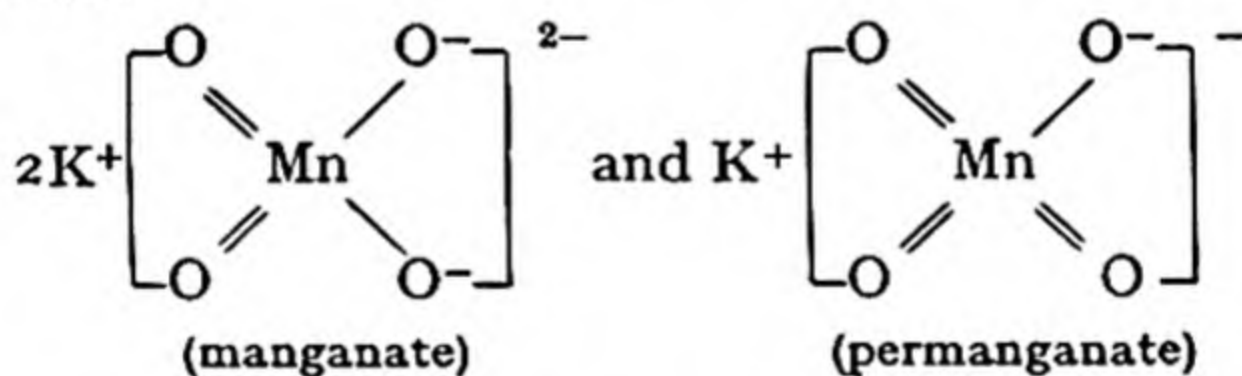
is, in fact, due to the anion MnO_4^- . A solution of sodium permanganate is put on the market as a disinfectant and antiseptic (*Condy's Fluid*).

Use of Potassium Permanganate in Volumetric Analysis. The fact that potassium permanganate quantitatively oxidizes a wide variety of substances makes it one of the most useful of volumetric reagents. Moreover, it is obtainable in a state of fairly high purity, and is not deliquescent; hence solutions of it for volumetric determinations are sometimes made up directly, when only moderate accuracy is required.

The theoretical basis of the necessary calculations following volumetric titrations with potassium permanganate is given in Chapter XVIII, p. 254.

A normal solution of potassium permanganate, when used in acid solution, contains 31.6 gm. KMnO_4 per litre. In practice, a decinormal solution, 3.16 gm. KMnO_4 per litre, is generally preferred. No indicator is necessary for the titration, since, on running in the permanganate, the colour is at first discharged. The titration is continued until addition of a drop of the permanganate results in a faint, permanent, pink colour. Excess of sulphuric acid (*not* hydrochloric acid, which may be oxidized) must be present.

Constitution of Manganates and Permanganates. The constitution of potassium manganate and potassium permanganate is believed to be as follows:



Uses of Manganese. The chief use of manganese is as a constituent of special steels and other alloys. Manganese steel, invented by SIR ROBERT HADFIELD in 1882, contains from 10 to 15 per cent of manganese, and is exceedingly tough. It is used for making rails that have to withstand very hard wear (e.g. points and cross rails); for the construction of safes and strong-rooms; for army helmets; and for many similar purposes. Manganese dioxide is used in the glass industry (p. 411), and as the depolarizer in dry cells (it slowly oxidizes the hydrogen liberated round the carbon anode). Potassium and sodium permanganates find wide application as antiseptics and disinfectants, and the potassium salt is used as an oxidizing agent for both qualitative and quantitative work.

Tests for Manganese.

1. Manganese compounds give an amethyst borax bead (oxidizing flame).
2. Fused with Na_2CO_3 (or NaOH) and a trace of KNO_3 : green mass of sodium manganate.
3. Manganous salts give
 - (a) with sodium hydroxide: a white precipitate of manganous hydroxide, $\text{Mn}(\text{OH})_2$, insoluble in excess but turning brown on exposure to air;
 - (b) with ammonium sulphide in neutral or alkaline solution: a buff or green precipitate of hydrated manganous sulphide, $\text{MnS} \cdot x\text{H}_2\text{O}$;
 - (c) on boiling with lead dioxide and aqueous nitric acid (in the absence of chlorides): a violet colour due to permanganic acid, HMnO_4 ;
 - (d) with ammoniacal silver nitrate spotted on to filter paper: a black stain of manganese dioxide and metallic silver:

$$\text{Mn}^{2+} + 2\text{Ag}[(\text{NH}_3)_2]^+ + 4\text{OH}^- =$$

$$2\text{Ag}\downarrow + \text{MnO}_2\downarrow + 4\text{NH}_3 + 2\text{H}_2\text{O}.$$

IRON, Fe

Atomic number: 26. Atomic weight: 55.85. Specific gravity: 7.9.
Melting-point: $1,535^{\circ}$. Boiling-point: $3,000^{\circ}$.

History. Meteorites consist largely of metallic iron, which has therefore been known from time immemorial. Methods of extracting it from its ores appear to have been first discovered in Asia, but iron-smelting was practised by the ancient Egyptians and other



FIG. 101. BLACKSMITHS IN THE TWELFTH CENTURY

nations of antiquity. Even as early as the twelfth century, the iron industry in England had become very considerable, and the Forest of Dean alone was able to provide 50,000 horseshoes for CŒUR DE LION's expeditionary force to Palestine. Among the alchemists, iron was known as Mars, from its supposed astrological connection with the planet. A relic of this nomenclature is to be found in the name *crocus martis*, still occasionally used to denote ferric oxide.

Occurrence. With the single exception of aluminium, iron is the most abundant of the metals, but very little of it is found free in the earth's crust. The principal iron ores are *haematite*,* Fe_2O_3 , *limonite*,† $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, *magnetite*,‡ Fe_3O_4 , *siderite*,§ FeCO_3 , and *clay iron-stone*, which is a mixture of siderite and clay. *Iron pyrites*,

* i.e. blood-like [stone], from its characteristic appearance.

† i.e. meadow [stone]. Greek, *leimon*, meadow.

‡ Some specimens are natural magnets (lodestones).

§ Greek, *sidēros*, iron.

FeS_2 (so called from the Greek *pyr*, 'fire,' because it will burn), is an abundant iron mineral, used principally as a source of sulphur and sulphur dioxide.

Rich iron-fields occur in Great Britain, United States, Scandinavia,

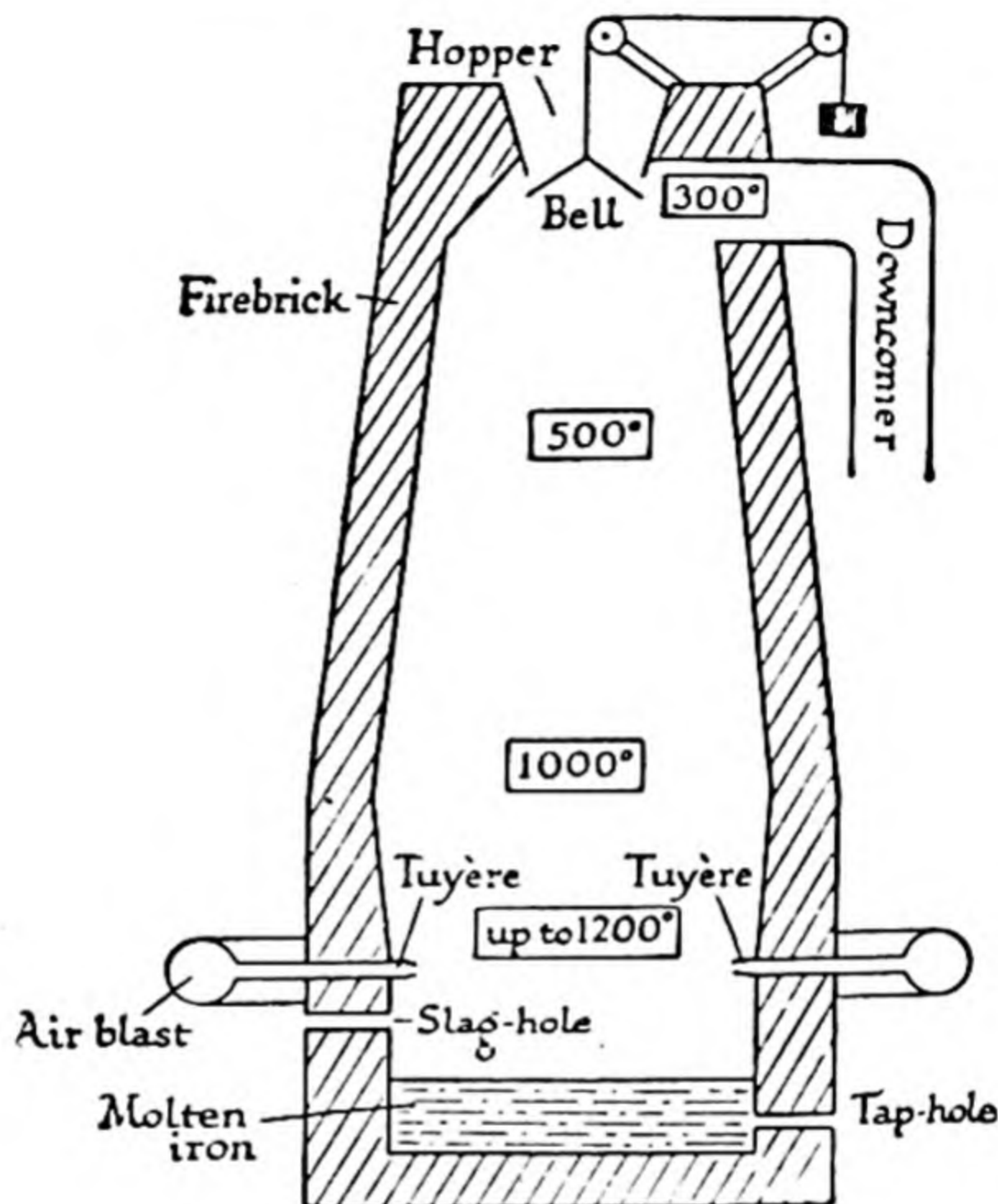


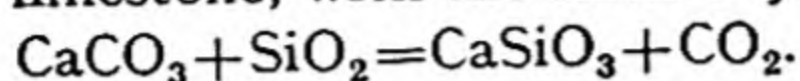
FIG. 102. BLAST FURNACE

Belgium, Spain (Bilbao), France (Alsace-Lorraine), Germany, China, and Brazil.

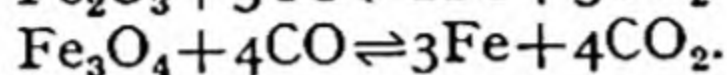
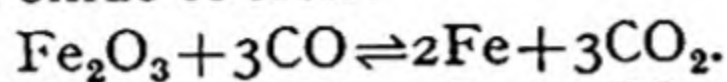
Extraction. Oxide ores may be reduced directly; carbonate ores are first roasted to convert the carbonate into oxide.

The reduction is carried out by means of coke in a blast furnace. This consists of a fire-brick tower, cased in iron and as much as 100 feet in height. The ore and coke are fed in at the top through a cone or bell hopper, and a regulated quantity of limestone (about half the weight of the coke) is added at the same time. The purpose of the limestone is to convert siliceous impurity in the ore into a fusible slag (calcium silicate, CaSiO_3), which may be drawn off from the bottom of the furnace; in this way the furnace can be worked

continuously. If the impurity in the ore is mainly calcareous, silica is added instead of limestone, with the same object:



A blast of hot air is forced up the furnace from pipes (*tuyères*, or *twyers*) near the bottom. The coke burns to carbon monoxide, and this reduces the iron oxide to iron:



The reaction is reversible, so that excess of carbon monoxide is necessary for complete reduction of the ore. The gases escaping from the furnace consequently contain a high proportion (24–25 per cent) of carbon monoxide and are burned either in special stoves (COWPER stoves) to heat the ingoing air blast, or in internal combustion engines to raise power for the blowers, etc.

The iron melts and runs to the bottom of the furnace, where it collects. The slag is less dense than the iron, and forms a second molten layer above the molten metal. The slag is discharged through the slag-hole, and the iron is run out through the tap-hole into sand moulds, where it solidifies into ingots called 'pigs.'

Pig-iron, otherwise known as *cast iron*, contains some 5 per cent of impurity, mostly carbon with smaller quantities of phosphorus, sulphur, and silicon. The carbon is partly free and partly in the form of iron carbide or 'cementite,' Fe_3C . Large amounts of pig-iron are used without further purification, since, as its alternative name implies, it can be cast in a variety of shapes by using appropriate moulds. It expands slightly on solidifying and thus reproduces the details of the mould; unfortunately, however, it is brittle and pieces of it cannot be welded together. The presence of impurities in cast iron give it a much lower melting-point than wrought iron or steel.

Wrought iron, or *malleable iron*, is made from cast iron by oxidation of the impurities, and is the purest commercial form of iron. The cast iron is melted on the hearth of a reverberatory furnace lined with haematite, the oxygen in which converts the carbon, silicon, sulphur, and phosphorus into their respective oxides. The gaseous oxides escape, while the silica forms a slag of iron silicate. As the impurities are removed, the melting-point of the iron rises, and the metal begins to solidify or become pasty. At this stage it is removed in lumps or 'blooms,' which are freed from slag by squeezing under steam-hammers.

Wrought iron contains less than 0.5 per cent of impurities, about half of which is carbon. It is tough, not brittle, and pieces of it can be welded together by hammering if heated to about $1,000^\circ$ (i.e. some four or five hundred degrees below its melting-point). Wrought

iron is used in making nails, horse-shoes, gates, ornamental iron-work, and other products of the smithy. It cannot be permanently magnetized and is therefore employed as the core in simple electro-magnets.

Steel is iron which contains from 0.15–0.5 (*mild steel*) or 0.5–1.5 per cent (harder steel) of carbon, mainly in the form of cementite, Fe_3C . In the BESSEMER process, it is made by pouring molten cast iron into a converter, mounted on a horizontal axis so that it can be tilted, and oxidizing the impurities with a blast of air introduced through twyers (Fig. 103). The carbon is oxidized to carbon monoxide, which burns at the mouth of the converter, while the oxides of silicon and phosphorus are absorbed in the lining of the converter. This lining consists of calcined dolomite (CaO.MgO), and the slag produced is sufficiently rich in phosphate to make it a valuable phosphate fertilizer ('basic slag'). The use of the dolomite lining was first suggested by THOMAS and GILCHRIST in 1879.

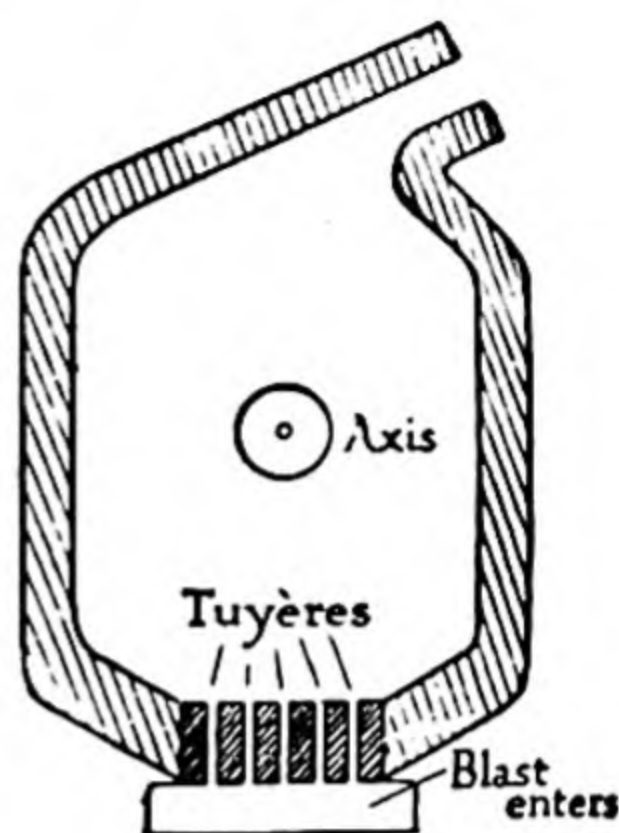


FIG. 103.

BESSEMER CONVERTER

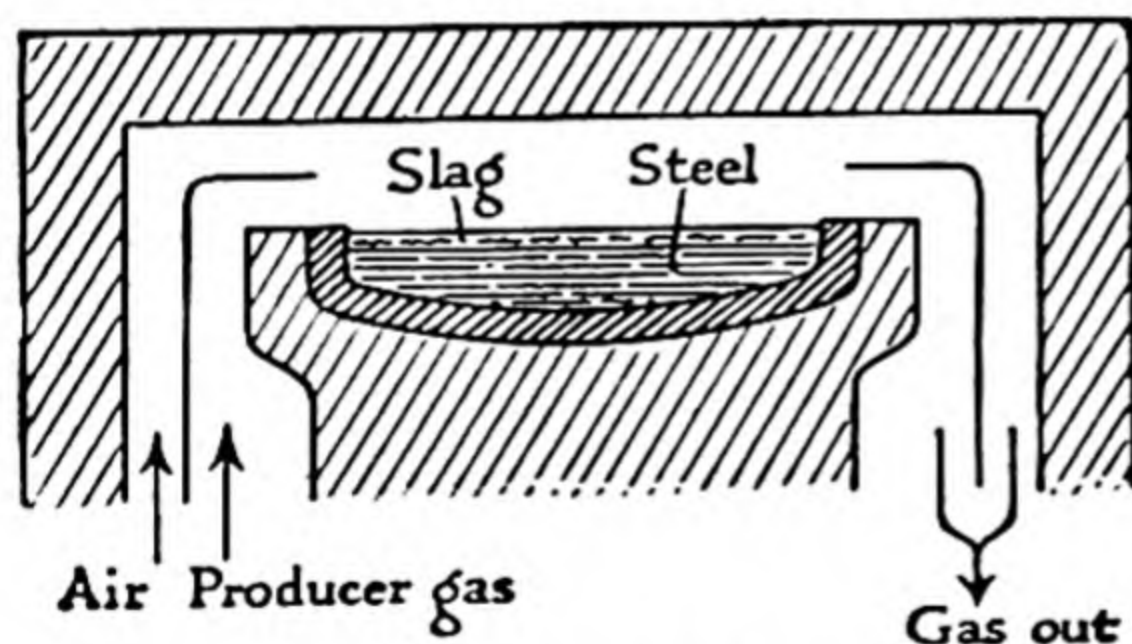


FIG. 104. SIEMENS OPEN-HEARTH FURNACE

In the SIEMENS-MARTIN, or *open-hearth*, process, cast iron is fused with scrap steel and just sufficient haematite to oxidize the excess of carbon and to bring the proportion of this element down to the required level. The open hearth on which the operation is conducted is lined with calcined dolomite and is heated by the combustion of producer-gas (p. 396).

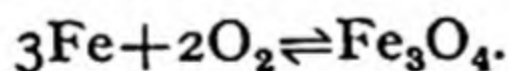
Properties of steel. The nature of steel depends partly upon its carbon content and partly upon its heat treatment. Steels with a low percentage of carbon are 'mild' or soft, and cannot be

The requisite amount of carbon is now added to the molten iron in the form of *spiegel*, or *spiegeleisen*, i.e. an alloy of iron, manganese, and carbon. The converter is then tilted and the steel poured into moulds.

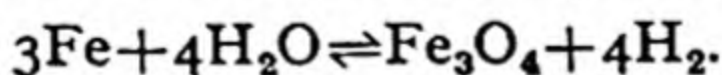
hardened. As the percentage of carbon increases, the steel becomes harder until the limit of 1.5 per cent is reached; beyond this point the metal is no longer steel but cast iron. Steel containing from 0.5 to 1.5 per cent of carbon can be given different degrees of hardness by heat treatment. If such steel is made red hot and plunged into cold water, it becomes excessively hard and brittle ('quenched steel'). If the quenched steel is then heated to various lower temperatures, the hardness is diminished but the toughness of the metal increases. This process is known as *tempering*, and can be followed by the eye, since the film of oxide formed on the surface assumes different colours at different temperatures. From 230° to 250° the colour is yellowish, and the steel then possesses a temper suitable for razor-blades, pocket-knives, etc. A blue colour develops at about 300°, and the temper of the steel is suitable for springs and chisels. Steel resembles wrought iron inasmuch as it is malleable and may be welded.

By alloying certain other substances with steel, *special steels* may be obtained with properties that render them very valuable for specific purposes. *Manganese steel*, containing 10–15 per cent of manganese, is extremely tough. *Silicon steel*, containing up to 5 per cent of silicon, is used in transformers, since it enormously reduces the waste of electrical energy. *Nickel steel* is used for armour-plate. *Chromium steel*, with 12–15 per cent of chromium, is the familiar stainless steel. *Chrome-tungsten steel* contains 2–6 per cent of chromium and 10–20 per cent of tungsten. It is very hard, and does not soften even at a red heat, a property which renders it invaluable for cutting- and drilling-tools (see also Chapter XXXII).

Properties of Iron. Iron is a white magnetic metal of specific gravity 7.9; it melts at 1,535°, and exists in three allotropic modifications, with transition points at 770°, 906°, and 1,400°. It is stable in dry air at ordinary temperatures, but burns if heated strongly enough, forming *triferric tetroxide*:

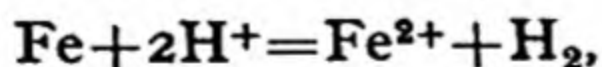


The same oxide is formed when steam is passed over white-hot iron:



In moist air under ordinary conditions iron rapidly rusts, a phenomenon considered more fully below.

Iron dissolves readily in dilute hydrochloric acid or dilute sulphuric acid, with evolution of hydrogen:



the other products being ferrous chloride or ferrous sulphate.

Dilute nitric acid dissolves it to form ferrous nitrate, $\text{Fe}(\text{NO}_3)_2$, oxides of nitrogen, and (sometimes) ammonium nitrate.

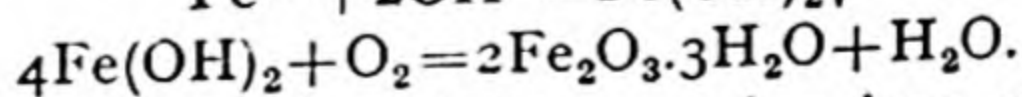
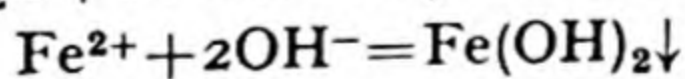
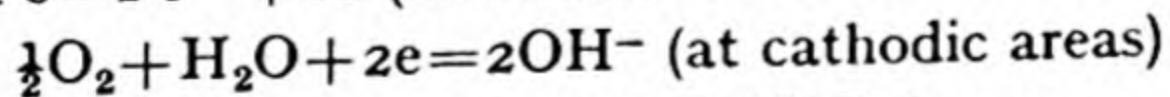
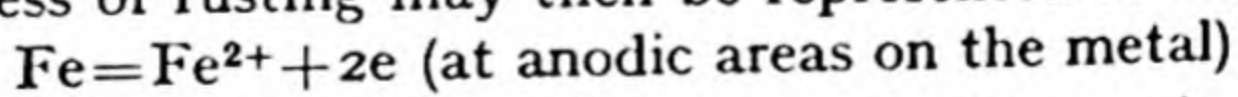
Concentrated nitric acid, and many other oxidizing agents, render iron *passive*; that is, they convert it into a condition in which it will no longer dissolve in dilute acids or displace copper from copper nitrate solution. Passivity is due to the formation of a thin coherent protective film of oxide; in fact, such a film has actually been removed from the surface of passive iron. Passivity is not permanent, and can easily be destroyed, e.g. by scratching or by heating in hydrogen.

Iron combines with chlorine, when heated in the gas, forming ferric chloride, FeCl_3 . It also combines readily with sulphur to give ferrous sulphide, FeS , and has the remarkable property of allowing hydrogen to pass through it, especially at high temperatures and pressures.

The *rusting of iron* is an electrochemical process, the essential change being the formation of ferrous ions, Fe^{2+} , from the metal. Ferrous compounds are easily oxidized to ferric compounds, and in this case the final product, rust, is chiefly a hydrated ferric oxide, $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. For rusting to take place, therefore, *water* (sufficient to form liquid on the surface of the metal, and not merely water-vapour) and *oxygen* are necessary. Even so, however, chemically pure iron will not rust if it is also physically homogeneous. Impurities in the iron render the metal liable to rust in the presence of water and oxygen, apparently because iron-particle and impurity-particle may form the poles of an electrolytic cell, enabling ferrous ions to pass into solution. Similar cells may apparently be set up between two particles of iron if their physical condition is sufficiently different.

The formation of ferrous ions is facilitated by increase of hydrogen-ion concentration in the water; hence the presence of carbon dioxide in rain-water causes iron to rust much more rapidly under natural conditions than when the water in contact with it is free from carbon dioxide.

The process of rusting may then be represented as follows:

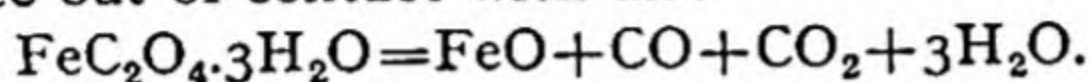


Rusting is normally prevented by covering iron objects with a coating impervious to water and air, e.g. vaseline, lanoline, paint, chromium-plate. The fact that rust is powdery, porous, and non-protective renders the rusting of iron very quick, fresh surfaces of the metal being continually exposed.

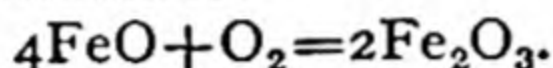
COMPOUNDS OF IRON: (i) FERROUS COMPOUNDS

In its chief compounds, iron is either bivalent (*ferrous* compounds) or trivalent (*ferric* compounds). Ferrates, e.g. BaFeO_4 , in which iron has valency VI, are known but are very unstable (cf. manganates).

Ferrous oxide, FeO , can be prepared by reducing ferric oxide in a current of hydrogen at 300° , and, in an impure form, by heating ferrous oxalate out of contact with air:

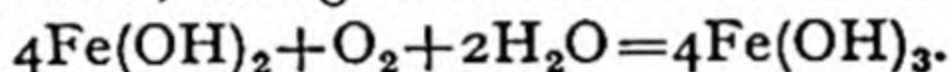


It is a black powder which on gentle warming oxidizes in the air to ferric oxide, with incandescence:

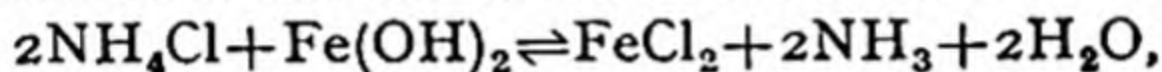


Ferrous oxide is a basic oxide, dissolving in dilute acids to form the corresponding salts containing the pale green ferrous ion, Fe^{2+} .

Ferrous hydroxide, $\text{Fe}(\text{OH})_2$, if precipitated in the complete absence of free oxygen is colourless. In the air it rapidly turns green and then brown, owing to oxidation to ferric hydroxide:

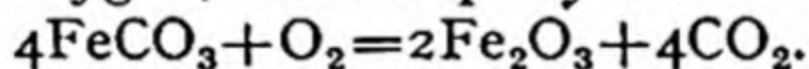


Ferrous hydroxide is soluble in ammonium chloride solution:

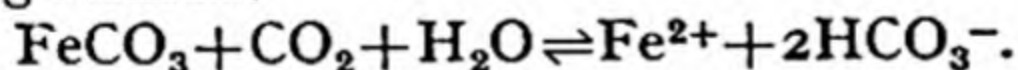


hence in Group III of the qualitative analysis tables the solution is boiled with a little nitric acid, to convert any ferrous iron into ferric iron, before the ammonium chloride and ammonia are added.

Ferrous carbonate, FeCO_3 , is also a white solid if precipitated in the absence of free oxygen, but is rapidly oxidized to ferric oxide:



It dissolves in water containing carbon dioxide, the soluble bicarbonate being formed:



Natural water containing ferrous bicarbonate is known as *chalybeate water* and is used for curative purposes. On exposure to air it deposits hydrated ferric oxide.

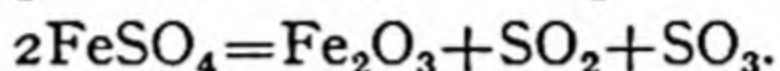
Ferrous chloride, FeCl_2 , is obtained anhydrous as colourless crystals when hydrogen chloride is passed over heated iron. From solutions of iron in dilute hydrochloric acid, pale green crystals of the *tetrahydrate*, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, may be obtained. Ferrous chloride is a strong reducing agent.

Ferrous sulphate heptahydrate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, formerly known as *green vitriol* or *copperas*,* is prepared commercially from the pickling

* Since it was prepared from a liquid *aqua cuprosa*, obtained in the manufacture of copper sulphate from copper pyrites.

tanks of dilute sulphuric acid used to clean iron sheets before galvanizing or plating. It can be made in the laboratory by dissolving iron in dilute sulphuric acid, but the solution must be evaporated in the absence of air (e.g. in a flask connected to the filter-pump) since oxidation readily occurs, especially in solution.

When the heptahydrate is heated, it loses six of its seven molecules of water of crystallization and forms the monohydrate. At 300° , the anhydrous salt is formed, and on further heating this decomposes into ferric oxide, sulphur dioxide, and sulphur trioxide:



By dissolving the sulphur trioxide in water, sulphuric acid can be made and this is indeed the method by which sulphuric acid was formerly manufactured at Nordhausen (Germany).

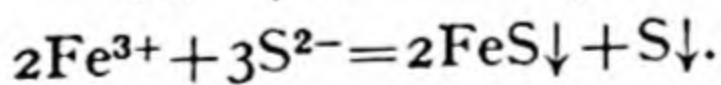
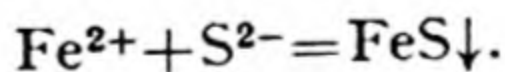
Ferrous sulphate heptahydrate is isomorphous with Epsom salt, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$.

With ammonium sulphate, ferrous sulphate forms the double salt *ferrous ammonium sulphate*, or *Mohr's salt*, $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$. This is much more resistant to oxidation than ferrous sulphate itself, and forms a convenient substance from which to prepare a standard solution of ferrous iron; it contains one-seventh of its weight of iron.

Ferrous sulphate is used as a weed-destroyer, and also in the manufacture of ink. When added to extract of nut-galls, ferrous sulphate gives a practically colourless solution of ferrous tannate. This is coloured with a blue dye, to make the characters written with it visible; and on exposure to air the ferrous tannate gradually oxidizes to ferric tannate, which is black. Hence the term 'blue-black' ink, and the difference in colour between old writing and writing freshly executed.

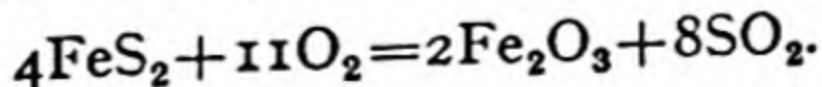
Ferrous sulphide, FeS , as commonly prepared by the direct combination of its elements, invariably contains free iron, so that hydrogen sulphide obtained by the action of dilute acid upon it is always contaminated with hydrogen.

Purer ferrous sulphide may be precipitated as an insoluble black substance on addition of an alkaline sulphide to a solution of a ferrous or a ferric salt:



On exposure to moist air, it is gradually oxidized.

Ferrous disulphide, FeS_2 , occurs in two mineral forms *iron pyrites* and *marcasite*,* which differ in crystalline form. It is largely employed as a source of sulphur dioxide, which it yields on roasting in air:

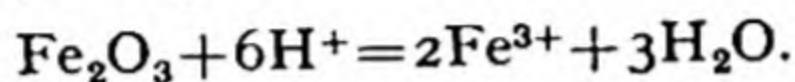


* Interesting as derived from the ancient Assyrian name of the mineral (*marhashi*).

COMPOUNDS OF IRON: (ii) FERRIC COMPOUNDS

Ferric oxide, Fe_2O_3 , occurs anhydrous as *haematite* (sometimes called 'kidney ore,' for a reason obvious on inspection of it), and hydrated as *limonite* and *rust*, both of which are $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. The residue of ferric oxide left after strongly heating ferrous sulphate is a fine powder known as *crocus martis*, *Venetian red*, *colcothar*, or *jeweller's rouge*; it is used as a pigment and a polishing powder for jewellery.

It is a basic oxide, dissolving, for example, in hydrochloric acid to form ferric chloride, FeCl_3 :

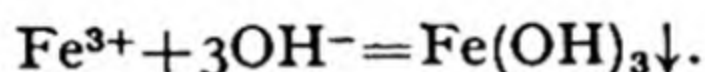


If required pure, it can be prepared by heating ferric hydroxide.

Ferroso-ferric oxide, triferric tetroxide, Fe_3O_4 , occurs naturally as magnetite and is often known as 'magnetic oxide of iron.' It is a typical 'mixed' oxide (see p. 492). On solution in hydrochloric acid it yields a mixture of ferrous and ferric chlorides.

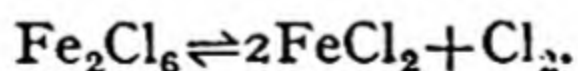
Triferric tetroxide is formed when the metal burns in air or oxygen, and when it is heated in steam. As may be gathered from its common name, it is strongly magnetic, though the natural mineral is not often already magnetized when mined.

Ferric hydroxide, $\text{Fe}(\text{OH})_3$, is thrown out of solution as a reddish-brown gelatinous precipitate when a solution of ammonia, caustic alkali, or sodium carbonate is added to a solution containing ferric ions:



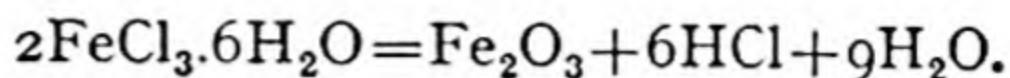
It is insoluble in water (though it readily forms a colloidal solution), and differs from aluminium hydroxide in being insoluble in excess of alkali. On standing, it quickly loses water, and on ignition yields ferric oxide.

Ferric chloride, FeCl_3 , is prepared anhydrous in the form of lustrous black scales—not unlike iodine—by heating iron in chlorine; the reaction is very exothermic and, once started, proceeds spontaneously. The vapour density of the chloride at about 450° corresponds to the double formula Fe_2Cl_6 , but at higher temperatures dissociation occurs into ferrous chloride and chlorine:

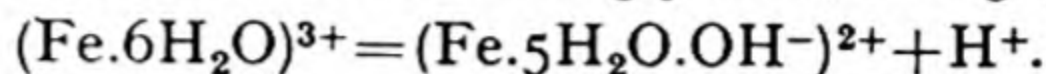


The anhydrous salt is very deliquescent, and very soluble in water, with which it forms a series of hydrates. The *hexahydrate*, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, may be obtained by evaporating a solution of ferric oxide in hydrochloric acid. It is a yellow deliquescent crystalline

solid. On heating, it loses water and hydrogen chloride, yielding a residue of ferric oxide:

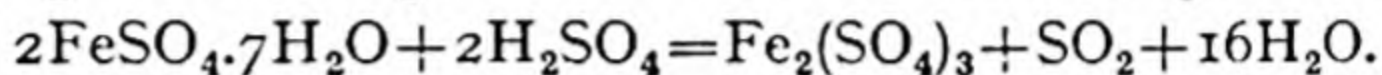


In solution, ferric chloride is strongly acid, owing to the reaction:



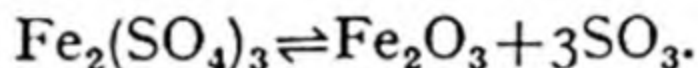
Ferric chloride results when chlorine is passed into a solution of ferrous chloride.

Ferric sulphate, $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$, is most conveniently prepared by heating ferrous sulphate with concentrated sulphuric acid:



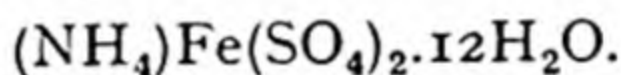
The anhydrous salt so prepared is dissolved in water and the solution concentrated, when the *enneahydrate* separates.

Strong heating decomposes ferric sulphate into ferric oxide and sulphur trioxide:



Ferric sulphate is formed as a by-product in the preparation of nitric oxide described on p. 442.

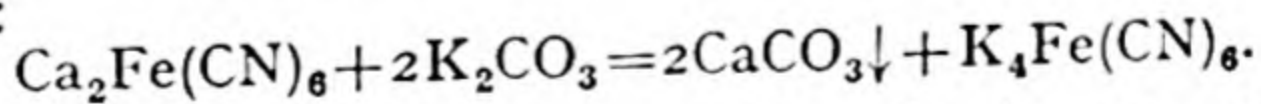
Ferric alum usually implies ferric *ammonium* alum,



This is a pale amethyst-coloured solid, isomorphous with the other alums.

COMPOUNDS OF IRON: (iii) COMPLEX COMPOUNDS

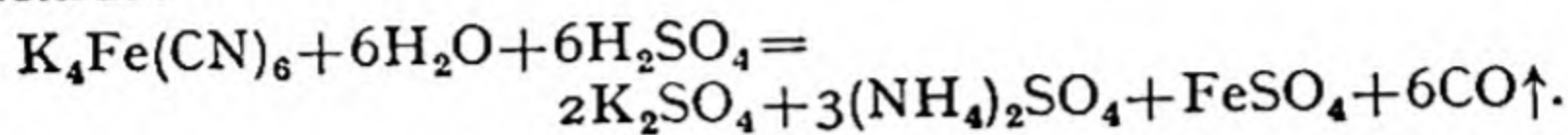
Potassium ferrocyanide, $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$, is a pale yellow crystalline solid formerly known as *yellow prussiate of potash*. It is manufactured by heating charred nitrogenous animal waste (e.g. horns, hooves, hides) with potassium carbonate and scrap iron, and extracting the mass with water. Further supplies are obtained as a by-product in the purification of coal-gas. The crude gas contains hydrogen cyanide, which is removed as ferrous and ferric cyanides, $\text{Fe}(\text{CN})_2$ and $\text{Fe}(\text{CN})_3$, by passing the gas through iron oxide. The cyanides react with ammonia (in the gas) to form Prussian blue (see below) and this is treated with lime to form calcium ferrocyanide, $\text{Ca}_2\text{Fe}(\text{CN})_6$. The calcium salt is dissolved in water and converted into potassium ferrocyanide by double decomposition with potassium carbonate:



Potassium ferrocyanide is a complex salt, its aqueous solution containing only the ions 4K^+ and $\text{Fe}(\text{CN})_6^{4-}$ and thus giving none of the reactions of ferrous ions (cf. p. 207). $\text{Fe}(\text{CN})_6^{4-}$ is the anion of

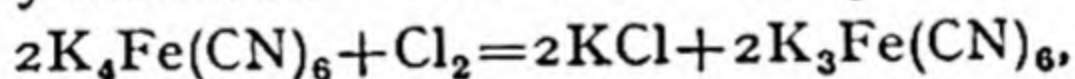
hydroferrocyanic acid, $\text{H}_4\text{Fe}(\text{CN})_6$, which may be obtained as colourless crystals by adding concentrated hydrochloric acid to a cold concentrated solution of potassium ferrocyanide, extracting with ether, and evaporating the ethereal solution.

When heated with dilute sulphuric acid, potassium ferrocyanide liberates hydrogen cyanide (hydrocyanic acid, 'prussic' acid, HCN), but with hot 60 per cent sulphuric acid it evolves carbon monoxide:

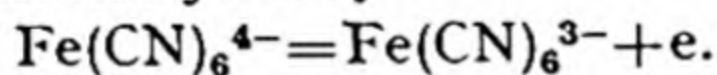


With a solution of a ferrous salt, potassium ferrocyanide gives a white precipitate of *potassium ferrous ferrocyanide*, $\text{K}_2\text{Fe}[\text{Fe}(\text{CN})_6]$; this rapidly turns blue, owing to oxidation to *potassium ferric ferrocyanide*, $\text{KFe}[\text{Fe}(\text{CN})_6]$. The latter compound is known as soluble Prussian blue, and is also obtained as a blue precipitate by adding a ferric salt to excess of potassium ferrocyanide solution. Sodium and ammonium ferrocyanides form similar blue precipitates with a ferric salt, the general formula being $\text{RFe}''[\text{Fe}''(\text{CN})_6]$, where $\text{R}=\text{K}, \text{Na}, \text{c. } \text{NH}_4$. According to KEGGIN and MILES, the iron atoms in Prussian blue are arranged, ferrous and ferric alternately, at the corners of a cubic lattice, and the CN groups lie in the edges of these cubes. The alkali metal atoms lie at the centres of alternate cubes. Lithium and caesium do not form Prussian blues, possibly because lithium atoms are too small, and caesium atoms too large, to enter the lattice easily.

Potassium ferricyanide, $\text{K}_3\text{Fe}(\text{CN})_6$, is made from potassium ferrocyanide by oxidation. This was formerly done with chlorine:



but is now effected electrolytically:

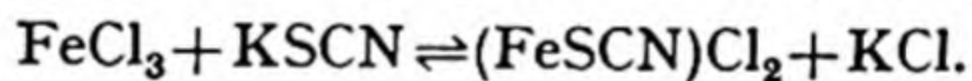


Potassium ferricyanide crystallizes in dark orange-red anhydrous crystals, formerly known as *red prussiate of potash*. It is somewhat unstable in the light, becoming coated with a film of the ferrocyanide, so that if a solution of ferricyanide free from ferrocyanide is required, the crystals should first be washed several times with distilled water.

With a solution of a ferrous salt, excess of potassium ferricyanide gives a blue precipitate, called 'TURNBULL'S blue' though it is actually the same as Prussian blue. With a solution of a ferric salt, potassium ferricyanide gives merely a brown coloration; this might be ascribed to the formation of soluble ferric ferricyanide, except for the fact that ferric ferricyanide is obtainable by the oxidation of Prussian blue and proves to be green in colour ('Berlin green').

Tests for Iron.

1. Borax bead: dark green (reducing flame) or reddish brown (oxidizing flame).
2. Fused with sodium carbonate on the charcoal block: magnetic powder of metallic iron.
3. Solutions of *ferrous* salts give with
 - (a) ammonia solution: greenish-white precipitate of ferrous hydroxide, $\text{Fe}(\text{OH})_2$, rapidly turning brown owing to oxidation;
 - (b) ammonium sulphide: black precipitate of ferrous sulphide, readily soluble in dilute acids;
 - (c) potassium ferricyanide: dark blue precipitate (Turnbull's blue).
4. Solutions of *ferric* salts give with
 - (a) ammonia solution: reddish-brown gelatinous precipitate of ferric hydroxide, $\text{Fe}(\text{OH})_3$;
 - (b) potassium ferrocyanide: dark blue precipitate (Prussian blue);
 - (c) potassium thiocyanate, KSCN : blood red coloration, probably due to a complex cation $(\text{FeSCN})^{2+}$:



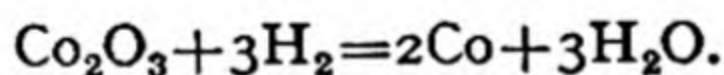
COBALT, Co

Atomic number: 27. *Atomic weight:* 58.94. *Specific gravity:* 8.8.
Melting-point: 1,480°. *Boiling-point:* 2,900°.

History. A certain mineral named *kibaltu* is mentioned in ancient Assyrian recipes for glass-making, and cobalt ores were used by the Assyrians and Egyptians in preparing blue glass and glaze. The name 'cobalt,' however, is usually supposed to be derived from the German *Kobold*, a mischievous subterranean gnome. Such gnomes haunted German copper mines, from which the miners occasionally obtained ores which on roasting gave an unpleasant smell and no copper. These false ores were called *kobold*, or *cobalt*, ores. BRANDT (1694–1768) showed in 1735 that cobalt ore contained a new metal, the properties of which were afterwards more fully investigated by BERGMANN (1735–84).

Occurrence. The principal deposits of cobalt ores—cobalt arsenide or *smaltite*, CoAs_2 , and a mixed arsenide and sulphide, *cobaltite*, CoAsS —are in the Congolese Republic, the Cobalt district of Ontario (Canada), Burma, and Rhodesia. The production from the last source has recently developed very considerably, with a corresponding fall in the price of the metal. Cobalt ores are always associated with nickel.

Extraction. The crushed and finely ground ore is smelted in a blast furnace with sand and limestone. The product, consisting of crude cobalt oxide, is dissolved in hydrochloric acid, and the cobalt precipitated again as the black hydrated sesquioxide ($\text{Co}_2\text{O}_3 \cdot x\text{H}_2\text{O}$) by the addition of bleaching-powder; any nickel remains in solution. The dried oxide is then reduced to metal by heating it in a current of hydrogen:



Pure cobalt is prepared by the electrolysis of an aqueous solution of pure cobalt sulphate, CoSO_4 , containing ammonium sulphate and a little ammonia.

Properties. Cobalt is a silvery-white, tough, and magnetic metal which is stable in air at ordinary temperatures, but burns if strongly heated, forming *tricobalt tetroxide*, Co_3O_4 . If heated in steam it is oxidized slowly to *cobaltous oxide*, CoO , hydrogen being set free.

Cobalt is readily attacked by dilute nitric acid, and less easily by dilute hydrochloric and sulphuric acids; concentrated nitric acid renders it passive (p. 590). It is not affected by alkalis.

Like nickel, cobalt forms a *carbonyl*, $\text{Co}_2(\text{CO})_8$; this is an orange crystalline solid (M.P. 52°), made by gently heating cobalt with carbon monoxide under a pressure of 30–40 atmospheres.

In its compounds, cobalt is usually either bivalent (cobaltous compounds) or trivalent (cobaltic compounds), but it may also be univalent.

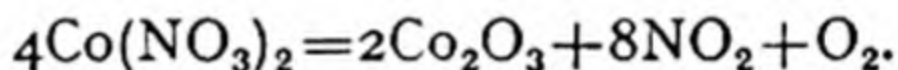
Uses. Cobalt steels have valuable magnetic properties and are used in making permanent magnets. Certain cobalt alloys, such as 'stellite' (Co, 55; W, 15-25; Cr, 25-15; Mo, 5 per cent), retain their hardness even at a red heat and are therefore useful as the material for drills and other high-speed tools. Cobalt compounds are employed to give a blue colour to glass.

COMPOUNDS OF COBALT

Oxides. Cobalt forms three definite oxides, viz. *cobaltous oxide*, CoO , *tricobalt tetroxide*, or *cobalto-cobaltic oxide*, Co_3O_4 , and *cobaltic oxide*, Co_2O_3 . The existence of a *dioxide*, CoO_2 , is doubtful.

Cobaltous oxide is a brown powder made by the careful reduction of cobaltic oxide in hydrogen at about $250^\circ\text{--}300^\circ$. It is a basic oxide, dissolving in dilute acids to form cobaltous salts containing the cobaltous ion Co^{2+} . On heating in the air, it is oxidized to tricobalt tetroxide.

Cobaltic oxide is obtained when cobaltous nitrate is moderately heated:



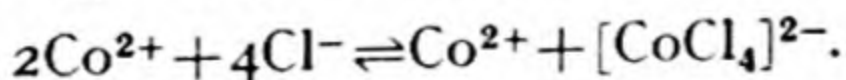
It is a brownish-black powder.

Tricobalt tetroxide is formed when either of the other oxides is strongly heated in the air, and when the metal is burned in air or oxygen. Like Fe_3O_4 it is a 'mixed' oxide.

Cobaltous Salts. Cobaltous salts are pink in solution, or when hydrated, but blue when anhydrous. The pink colour is that of the hydrated ion $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$.

Cobaltous chloride, CoCl_2 , is formed as blue anhydrous scales when cobalt is heated in chlorine. Solutions of the oxide, hydroxide, or carbonate in dilute hydrochloric acid are pink and on crystallization yield the raspberry-coloured hexahydrate, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. This can be dehydrated by heat.

An aqueous solution of cobaltous chloride turns blue on concentrating, on heating, and on the addition of hydrochloric acid, potassium chloride, sodium chloride, calcium chloride, or alcohol. If the blue solution is diluted, the pink colour is restored. A complex anion $(\text{CoCl}_4)^{2-}$ is probably the cause of the blue colour:



If cobaltous chloride is dissolved in alcohol, the solution is blue;

addition of zinc chloride or mercuric chloride turns it pink. The explanation advanced in this case is that zinc and mercury have a greater tendency to form complex anions than cobalt itself; hence the change $(\text{CoCl}_4)^{2-} + \text{Zn}^{2+} = \text{Co}^{2+} + [\text{ZnCl}_4]^{2-}$ takes place with the zinc chloride and a similar change with the mercuric chloride. WARDLAW and PERCIVAL have isolated salts containing the anion $[\text{CoCl}_4]^{2-}$.

A solution of cobaltous chloride is used as invisible ink. When the 'ink' dries, the pale pink colour of the hexahydrate is scarcely perceptible; but, on heating, the deep blue colour of the anhydrous salt becomes apparent. A moist sigh over affecting passages will make them disappear again.

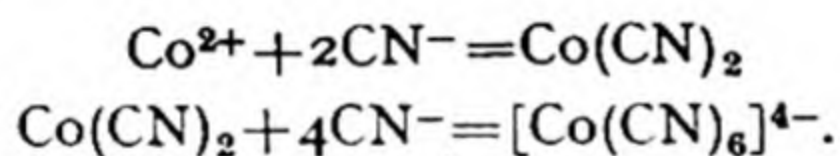
Cobaltous carbonate, CoCO_3 , is precipitated as a pink solid when sodium bicarbonate solution is added to a solution containing cobaltous ions:



Sodium carbonate precipitates a basic carbonate.

Cobaltous sulphate, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, is isomorphous with nickel sulphate.

Cobaltous cyanide, $\text{Co}(\text{CN})_2$, is formed as a pinkish-brown precipitate when potassium cyanide is added to a solution of a cobaltous salt. It is soluble in excess, owing to formation of the complex cobaltocyanide ion, $[\text{Co}(\text{CN})_6]^{4-}$:



Cobaltocyanides, such as the potassium salt, $\text{K}_4\text{Co}(\text{CN})_6$, are readily oxidized to the cobalticyanides, e.g. $\text{K}_3\text{Co}(\text{CN})_6$ (isomorphous with potassium ferricyanide, $\text{K}_3\text{Fe}(\text{CN})_6$).

Cobaltic Salts. The simple cobaltic salts are comparatively little known, but complex cobaltic ions are readily formed with ammonia (cations) or CN^- and NO_2^- ions (anions). The ammonia compounds are known as *cobaltamines*; a typical example is hexamminocobaltic chloride, $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, which ionizes into $[\text{Co}(\text{NH}_3)_6]^{3+}$ and 3Cl^- . Chloropentammino-cobaltic chloride, $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$, gives the ions $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ and 2Cl^- , which explains the way in which it is formulated.

Potassium cobaltinitrite, $\text{K}_3[\text{Co}(\text{NO}_2)_6]$, is obtained as a yellow precipitate by adding sodium cobaltinitrite to a solution of a potassium salt. Its formation is used as a test for potassium, but since ammonium and magnesium yield similar precipitates they must be removed before the test is applied.

Tests for Cobalt.

1. Borax bead: blue.
2. Solutions of cobaltous salts give with
 - (a) sodium hydroxide in the cold: blue precipitate of a basic salt. On warming, pink cobaltous hydroxide, Co(OH)_2 , is formed;
 - (b) ammonium sulphide: black precipitate of cobaltous sulphide, CoS , insoluble in excess of reagent (distinction from nickel);
 - (c) potassium cyanide: pinkish-brown precipitate of cobaltous cyanide, soluble in excess to form a brownish solution of the cobaltocyanide.

NICKEL, Ni

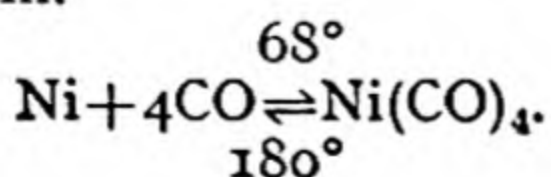
Atomic number: 28. *Atomic weight:* 58.71. *Specific gravity:* 8.9.
Melting-point: 1,455°. *Boiling-point:* 2,900°.

History. 'Nickel' is a German equivalent of the English 'Old Nick,' or the devil. Certain ores which, like cobalt ores (p. 597), resembled copper ores but yielded no copper were described by the medieval German miners as *Kupfernickel*, i.e. 'Old Nick's copper.' From them, nickel was extracted in 1751 by CRONSTADT (1722-65)—who is also remembered as the inventor of blowpipe analysis. Nickel and its compounds were more fully studied by BERGMANN (1775).

Occurrence. Nickel occurs native in meteorites, where it is associated with iron. Its chief ores are *pentlandite*, NiFe_2S_3 , *smaltite*, $(\text{Ni}, \text{Co}, \text{Fe})\text{As}_2$, and *garnierite*, a hydrated nickel magnesium silicate. The bulk of the annual nickel output comes from the pentlandite deposits at Sudbury, Ontario.

Extraction. The extraction of nickel from *pentlandite* is a highly technical process, the details of which lie beyond the scope of this book. In outline, it is as follows. The ore is first concentrated by flotation (p. 353) and then roasted in the air, to remove much of the sulphur and to convert the iron into iron oxide. The roast is next smelted with a flux, when the iron forms a slag of iron silicate, and a residual 'matte' of mixed nickel sulphide and copper sulphide is obtained.

The matte is ground, roasted in the air to oxidize it, and extracted with hot dilute sulphuric acid; this dissolves out the copper oxide but leaves the nickel oxide. The nickel oxide is now subjected to the MOND carbonyl process. It is heated to 340° in water-gas (p. 396), the hydrogen in which reduces it to metallic nickel. At a lower temperature (68°), the carbon monoxide combines with the nickel to form nickel carbonyl, $\text{Ni}(\text{CO})_4$, which at this temperature is a gas (B.P. 43°) and passes off in the stream of carbon monoxide, all impurities in the crude nickel being left behind. The mixture of carbon monoxide and nickel carbonyl is passed into a tower filled with nickel pellets and maintained at a temperature of 180°; here the carbonyl is decomposed, and the pellets grow in size by the deposition of pure nickel upon them. The carbon monoxide is recovered and used again.

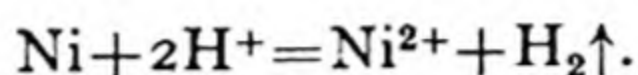


Properties. Nickel is a white, malleable, and ductile metal of

iron-like hardness. It melts at $1,455^{\circ}$, boils at $2,900^{\circ}$, and has a specific gravity of 8.9. Like iron, it can be welded and magnetized, though its magnetic powers are not very strong.

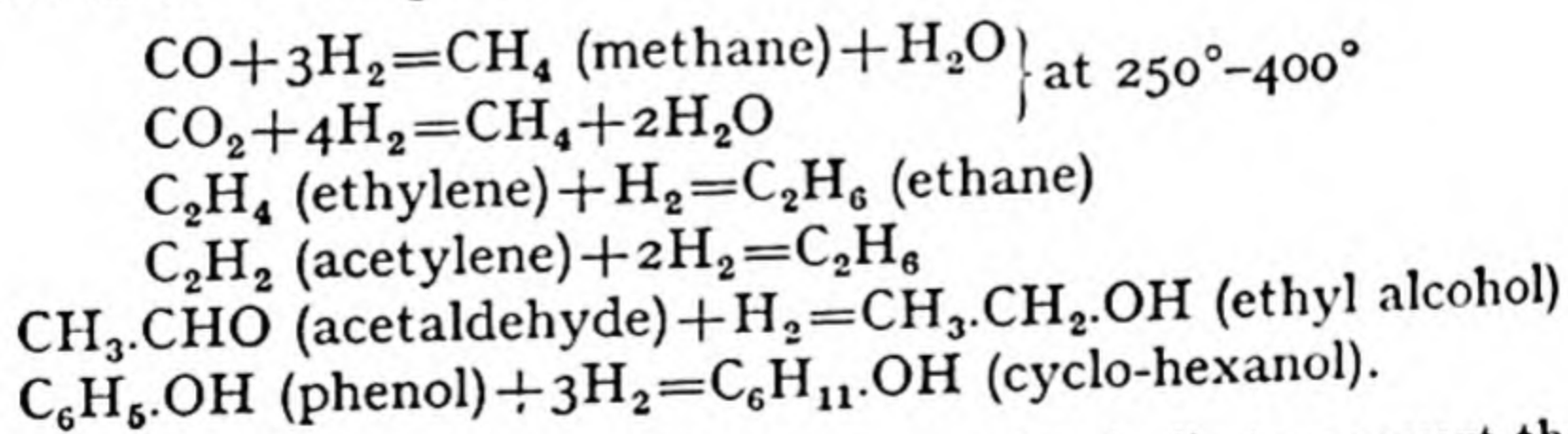
In the air, nickel tarnishes fairly slowly, hence its former popularity as a plating metal. When finely divided, however, it oxidizes with great ease and vigour, sometimes becoming red-hot spontaneously; the product is *nickelous oxide*, NiO .

Dilute hydrochloric acid and dilute sulphuric acid slowly dissolve nickel, forming *nickelous chloride* or *nickelous sulphate* with evolution of hydrogen:



Concentrated nitric acid renders it passive; more dilute acid converts it into the nitrate, oxides of nitrogen being evolved. It is very resistant to alkalis.

Uses. Though nickel-plating has been largely superseded by chromium-plating, nickel has many and varied applications. One of the most interesting is catalytic, for, at temperatures generally ranging from about 200° to 300° , it is extraordinarily efficient in catalysing the reduction of organic compounds by gaseous hydrogen. This property was discovered by the French chemists SABATIER and SENDERENS. The nickel is usually employed in the form of 'reduced nickel,' i.e. nickel in a very fine state of division prepared by reducing nickelous oxide in hydrogen—preferably at the same temperature as that at which it is to be used for the catalysis. The organic compound, in the state of gas or vapour, is mixed with hydrogen, and the mixture is passed over the gently heated reduced nickel; in most cases the yield of product is very high, and in many cases almost theoretical. *Examples:*



In the hydrogenation of vegetable or animal oils to convert them into fats (p. 277), the nickel is employed in the form of shavings, not powder.

Nickel is a constituent of many important alloys, one of the principal of which is *Monel metal*, so called after AMBROSE MONELL, a former president of the International Nickel Company. Large quantities of nickel ore in the Sudbury district contain a relatively high percentage of copper, and since the separation of the two

metals in these circumstances is both difficult and expensive, it was decided to smelt them together and to see whether the alloy so obtained had any commercial value. The result surpassed all expectations; further experiments were made, and it was ultimately found that an alloy containing 65 per cent of nickel, 32 per cent of copper, 1.5 to 2.5 per cent of iron, 0.5 to 1 per cent of manganese, and small but carefully controlled amounts of carbon, sulphur, and silicon, gave the best results. Monel metal is essentially a solid solution of copper in nickel. It has great tensile strength, is not seriously weakened even at 400° , can be cold-worked without becoming brittle, is not corroded appreciably by the air, and withstands the action of sea-water, alkalis, and ammonia. It is widely used in a great variety of industries.

Invar is an alloy of about 35 per cent nickel with a little manganese and carbon and the rest iron. It has an exceedingly small coefficient of expansion and is therefore used in making clock pendulums, measuring rods, and similar apparatus. *Nichrome* contains about 60 per cent of nickel, 26 per cent of iron, and 14 per cent of chromium; it has a high resistance and melting-point and is consequently employed as resistance wire and for electric heaters. A nickel alloy formerly very popular is *German silver*, which contains some 25 per cent of nickel, 55 per cent of copper, and 20 per cent of zinc; it was used chiefly for plate and ornaments. Cupro-nickel coinage alloy usually contains about 25 per cent of nickel and 75 per cent of copper.

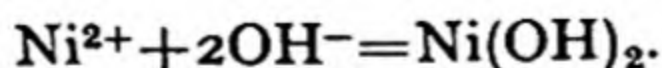
For nickel steel, see p. 589.

COMPOUNDS OF NICKEL

Nickel is zero-valent in its carbonyl, and in a few compounds, e.g. $\text{Ni}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ (hydrated nickelic oxide), it is tervalent. In the vast majority of its compounds, however, it is bivalent, and the only simple ion it produces in solution is the green *nickelous* ion $\text{Ni}^{2+} \cdot (6\text{H}_2\text{O})$: the anhydrous ion Ni^{2+} is yellow.

Nickelous oxide, NiO , is a greenish solid prepared by gentle ignition of the hydroxide or carbonate, or by passing steam over the red-hot metal. It is a basic oxide, reacting with acids to form nickelous salts.

Nickelous hydroxide, $\text{Ni}(\text{OH})_2$, separates as a green gelatinous precipitate when a solution of a caustic alkali is added to a solution of a nickelous salt:



If excess of alkali is added, the precipitate does not dissolve; on addition of bromine to the alkaline suspension, however, a black
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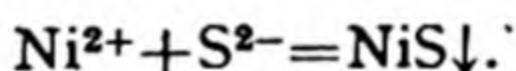
substance is formed. This is stated by various chemists to be (a) nickelic hydroxide, $\text{Ni}(\text{OH})_3$, (b) hydrated nickelic oxide, $\text{Ni}_2\text{O}_3 \cdot \text{H}_2\text{O}$, (c) hydrated nickel dioxide, $\text{NiO}_2 \cdot x\text{H}_2\text{O}$, (d) a mixture of nickelous oxide, NiO , and hydrated nickel dioxide: from which the reader will gather that its composition is uncertain. Its importance lies in the fact that it is precipitated when alkali and bromine (i.e. hypobromites) are added to a solution of potassium nickelocyanide (see below), while the corresponding cobaltocyanide (p. 599) remains in solution, as cobalticyanide, under similar conditions. This affords a means of separating nickel from cobalt.

With ammonia solution, a solution of a nickelous salt yields a green precipitate—probably the hydroxide—but this readily dissolves in excess, forming a blue solution containing the complex ion $\text{Ni}(\text{NH}_3)_6^{2+}$ or $\text{Ni}(\text{NH}_3)_4^{2+}$. In the presence of ammonium salts, ammonia does not give a precipitate with a nickelous solution.

Nickelous carbonate, NiCO_3 , is a pale green solid precipitated from a solution of a nickelous salt by addition of sodium bicarbonate; sodium carbonate yields a basic nickelous carbonate.

Nickelous sulphate, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, is a green crystalline solid; the anhydrous salt is yellow. The double salt *nickelous ammonium sulphate*, $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, is used as the electrolyte in nickel-plating; the anode is a nickel block, while the cathode consists of the object to be plated.

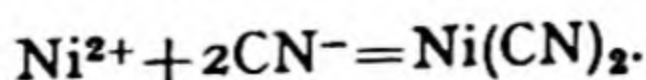
Nickelous sulphide, NiS , is obtained as a black precipitate when a sufficiently high concentration of sulphide ions, S^{2-} , is formed in a solution of nickelous salt:



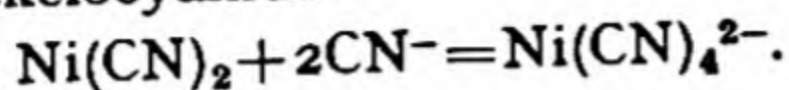
This cannot be effected in acid solution, hence nickel is not precipitated in Group II; it is, however, brought about by the use of ammonium sulphide, and nickel thus appears in the same group as zinc, manganese, and cobalt. The remarkable fact that precipitated nickelous sulphide is only partially soluble in dilute acids is ascribed to the immediate transformation of some of the precipitate into a more complex form.

Nickelous chloride, NiCl_2 , can be prepared as a yellow anhydrous solid by passing chlorine over the strongly heated metal. It dissolves in water to form a green solution, from which the green *hexahydrate* can be crystallized out. If the hexahydrate is heated in the air it yields a residue of a basic salt, but it can be dehydrated without hydrolysis in a stream of hydrogen chloride.

Nickelous cyanide, $\text{Ni}(\text{CN})_2$, is precipitated by potassium cyanide from a solution of a nickelous salt:



It is a green substance, soluble in excess of potassium cyanide to form potassium nickelocyanide:

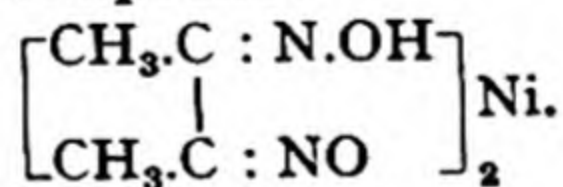


Nickel carbonyl, Ni(CO)_4 , has been mentioned on p. 601. It is a colourless, extremely poisonous liquid (B.P. 43° , M.P. -25°). On heating, it decomposes into nickel and carbon monoxide at about 180° ; if suddenly heated to higher temperatures it explodes.

Tests for Nickel Salts.

1. Hydrated nickel salts are usually green and the anhydrous salts yellow.
2. Sodium hydroxide solution with a solution of a nickel salt yields a green precipitate of nickel hydroxide, Ni(OH)_2 , insoluble in excess of sodium hydroxide.
3. Ammonium sulphide gives a black precipitate of nickel sulphide, NiS .
4. Aqueous ammonia produces a green precipitate; this is the hydroxide (or a basic salt) and is soluble in excess of reagent ammonia solution, owing to the formation of the blue complex ion $[\text{Ni(NH}_3)_6]^{2+}$.

5. An alcoholic solution of dimethylglyoxime, $\text{CH}_3\text{.C : N.OH}$
 $\text{CH}_3\text{.C : N.OH}$
 added to a solution of a nickel salt which is then made faintly alkaline with aqueous ammonia, gives a bright red precipitate consisting of the compound:



(Distinction from cobalt.)

6. In the oxidizing flame, nickel compounds colour the borax bead brown.

COMPARATIVE EXERCISES

1. Compare and contrast the properties of chromium with those of (a) aluminium, (b) manganese, (c) iron.
2. Compare and contrast the properties of nickel with those of cobalt, and, after reading Chapter XXIII, 'Copper,' with those of copper.

CHAPTER XXXII

BERYLLIUM, TITANIUM, GERMANIUM, MOLYBDENUM, TUNGSTEN

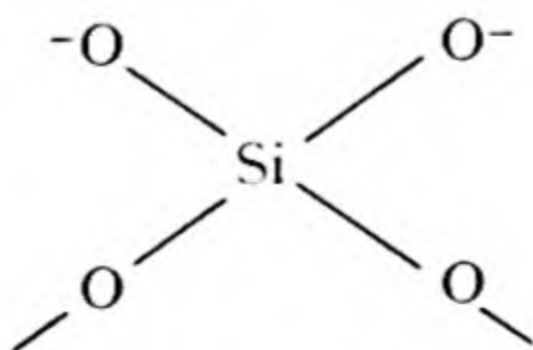
IN RECENT years scientific progress has stimulated the extraction and marketing of a number of elements previously little used on the industrial scale. At present most of such elements are employed in their elementary forms, and therefore in the following brief accounts of some of them a detailed treatment of their compounds has not been attempted.

BERYLLIUM, Be

Group IIA. Atomic number: 4. Atomic weight: 9.013. Specific gravity: 1.84. Melting-point: 1,280°.

Historical. The Abbé HAUY (1743-1822), whose ideas on the structure of crystals helped to found the science of crystallography, had noticed a close similarity between the crystal form and other physical properties of the mineral *beryl* and the gem-stone *emerald*. Analyses made at his suggestion by VAUQUELIN in 1798 proved not only the identity of their chemical composition but that each contained a new metallic element of which Vauquelin isolated the oxide (or 'earth'). On the ground that some of its salts tasted sweet the oxide was named '*glucina*,' and the metal, prepared by WÖHLER in 1828, was called *glucinum*, and assigned the symbol Gl. This name and symbol persist to-day in French treatises, but elsewhere the name *beryllium* (symbol Be) has long been preferred.

The composition of beryl, a double silicate of beryllium and aluminium, may be formulated ionically as $(\text{Be}_3\text{Al}_2)^{12+} \cdot (\text{Si}_6\text{O}_{18})^{12-}$. The anion is a structure formed from six of the units

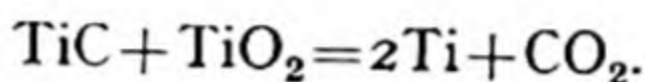


each carrying charge 2^- , united in a closed ring. Emerald is beryl coloured by a trace of chromic oxide, Cr_2O_3 .

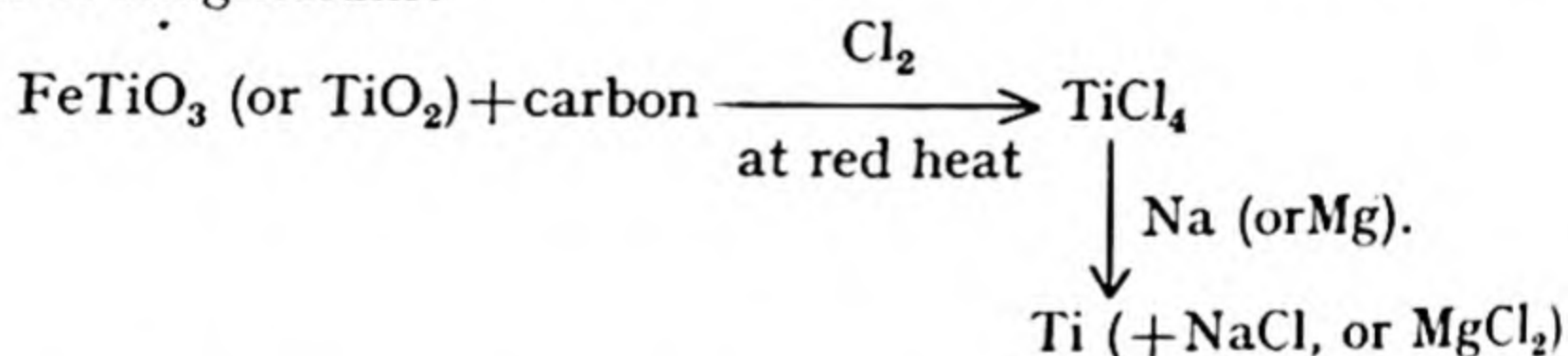
TITANIUM, Ti

Group IVA. Atomic number: 22. Atomic weight: 47.90. Specific gravity: 4.5. Melting-point: 1,725°.

Historical. Although recognized as an element in Cornish ilmenite during the last decade of the eighteenth century, the metal was first isolated in reasonably pure form by MOISSAN in 1895. After obtaining the carbide TiC by heating the dioxide TiO₂ and carbon in an electric furnace, addition of a further appropriate quantity of dioxide yielded the metal contaminated with only a small amount of carbon:



Sources and Extraction. Titanium is one of the most abundant metals in the earth's crust, but it is very widely distributed in small concentrations, and workable ores are relatively uncommon (see p. 85). The principal sources are *ilmenite* or 'titaniferous iron ore,' FeTiO₃, and *rutile*, the dioxide TiO₂. The modern method of producing the metal depends on the intermediate isolation of the volatile tetrachloride, TiCl₄ (B.P. 136°), and its reduction with sodium or magnesium:

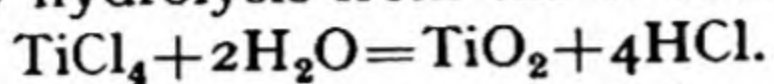


After leaching out soluble chloride the crude metal is obtained as a grey powder, which, mixed with iodine, is placed in an evacuated chamber heated to about 200°, and traversed by tungsten wires electrically heated to 1,000°. On these the volatilized tetra-iodide is locally dissociated and rods of the pure metal develop round the heated wires. The metal so prepared is malleable and ductile; its melting-point is 1,725°.

The Uses of Titanium. The pure metal has admirable properties for structural services. It has a very high tensile strength and a density (4.5 gm./c.c.) little more than half that of steel, over which it has therefore much advantage in strength/weight ratio, which is the significant quantity concerned. Further, its resistance to corrosion, even at relatively high temperatures, and by sea-water, is comparable with that of 'stainless' steels. Its rich potentialities

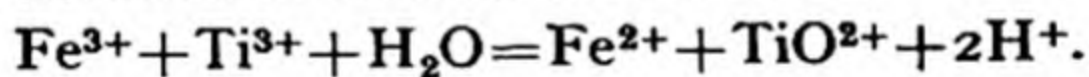
cannot however be fully realized until a cheaper large-scale method of production of the pure metal has been devised.

At present nearly all titanium extracted from its ores passes into industry as 'titanium white,' the finely divided dioxide, TiO_2 , readily obtained by hydrolysis from the tetrachloride:



As a pigment titanium dioxide is non-poisonous, unaffected by sulphur compounds in the air, and has a superior covering power to 'white lead,' which it has rapidly replaced in the paint industry. It has further important uses in the manufacture of white paper, and in the production of vitreous enamels.

Titanium Compounds. In the typical and colourless compounds TiO_2 and TiCl_4 titanium exerts the group quadrivalency, but it can also exist in a tervalent state, then giving rise to the *titinous* series of compounds, of which the best known are the chloride TiCl_3 and the sulphate $\text{Ti}_2(\text{SO}_4)_3$. Unlike the tetrahalides, which are volatile and covalent and violently hydrolysed by water (cf. SiCl_4), the titanous compounds are typical salts, i.e. ionic compounds. They yield violet-purple aqueous solutions which possess strong reducing properties. Titanous chloride is often used in volumetric analysis for the direct titration of iron in the ferric state:



GERMANIUM, Ge

Group IVB. Atomic number: 32. Atomic weight: 72.60. Specific gravity: 5.35. Melting-point: 960°. Boiling-point: 2,700°.

Historical. MENDELÉEFF, in 1871, predicted the existence of a then unknown element, 'eka-silicon,' lying in Group IV of the periodic system between silicon and tin (p. 77). The prediction was verified in 1886 when C. WINKLER discovered and named *germanium*.

Sources and Extraction. Germanium is widely distributed, mostly as the disulphide GeS_2 , in small concentrations, especially in zinc sulphide ores. The only ore used commercially at present as a source of the element is *germanite*, from S.W. Africa. This mineral is a complex mixture principally of the sulphides of copper, iron, arsenic, and germanium, containing 5–8 per cent of the last. On heating crushed germanite in a stream of hydrogen chloride the volatile GeCl_4 (B.P. 83°) is produced and collected. After purification by fractional distillation the chloride is hydrolysed to give GeO_2 (cf. TiCl_4 , p. 609), which is then reduced to metal by hydrogen, carbon, or KCN acting under a flux of fused salt.

Almost all germanium produced is employed in the manufacture of *transistors*, electrical devices which are advantageously replacing thermionic valves.

For this purpose an extremely pure form of the metal is essential, and is obtained by 'zone refining.' This process consists in passing an annular electric heating unit along a rod of the metal so that short lengths are brought successively to fusion (M.P. 960°) as the heating unit is moved slowly forward. Impurities tend to collect in the liquid zone, and are finally transferred to a short terminal length, which is discarded.

Properties of Germanium. Crystalline germanium is a very brittle solid resembling 'white' tin in colour: it is not corroded at ordinary temperature on exposure even to moist air. On heating to redness in air or oxygen contained in a closed vessel the volatile, jet-black monoxide, GeO , sublimes, while the colourless dioxide, GeO_2 , forms a deposit upon the element. Like silicon (and 'grey' tin) germanium has the macromolecular diamond structure, in which every atom is linked tetrahedrally to four others (p. 388) and is a *semi-conductor* of electricity.

Semi-conductance differs from metallic conductance mainly in the following respects:

Semi-conductors

- (i) Conductance *increases* rapidly with rise of temperature:
- (ii) Conductance is vastly enhanced by the presence of even traces of suitable impurities.

Metallic conductors

Conductance *decreases* with rise of temperature:

Conductance not greatly affected by small amounts of impurity, but is usually somewhat *decreased*.

At ordinary temperature pure silicon and germanium are practically non-conductors (sp. conductance $\approx 10^{-6}$ mho/cm.), but at 600° germanium conducts about as well as bismuth. The presence in silicon of one atom of elementary boron per million atoms of silicon increases the conductance at ordinary temperature by a factor of about 10^5 . The use of germanium in transistors depends upon such effects of traces of other elements deliberately added to the element purified by zone-refining.

Compounds of Germanium. Resembling tin, germanium forms two series of compounds in which it is respectively *bivalent* and *quadrivalent*. The most stable of the germanous compounds is the sulphide, GeS ; with hydrogen chloride germanous chloride, GeCl_2 , yields *germanochloroform*, GeHCl_3 , analogous to chloroform, CHCl_3 , and silicochloroform, SiHCl_3 . In its quadrivalent state germanium forms several volatile hydrides, of which the simplest, *monogermane*, GeH_4 , is gaseous, with B.P. -90° (cf. silicon hydrides, p. 407). In respect to the position of germanium in Group IV, intermediate between silicon and tin, it is interesting that the dioxide, GeO_2 , is dimorphous, one form being similar in crystal structure to quartz, SiO_2 , and the other to cassiterite, SnO_2 .

MOLYBDENUM, Mo

Group VIA. Atomic number: 42. Atomic weight: 95.95. Specific gravity: 10.2. Melting-point: 2,620°.

Historical. The name of this metal has an interesting etymological history. The Latin name *molybdaena*, derived directly from the Greek *molybdos*, meaning metallic lead, was originally applied to a variety of soft, black minerals which, in common with lead itself, left a mark when rubbed on paper. The Latin name for lead, *plumbum*, was probably a corruption of *molybdos*, and the old names for graphite, *plumbago* or *black lead*, are still occasionally used. Amongst the many bodies included by the term *molybdaena* was the mineral now called *molybdenite*, MoS_2 , which is strikingly similar in appearance and in some physical properties to graphite. These two materials were not distinguished chemically until, in 1779, SCHEELÉ proved molybdenite to be the sulphide of a then unknown metal, isolated in 1782, and named *molybdenum*.

Extraction. To-day molybdenite remains the principal source of the metal. On roasting in air it is converted into the colourless, acidic oxide MoO_3 . Over 90 per cent of all molybdenum at present produced is used in alloy steels, and for this purpose the oxide is mixed with ferric oxide and submitted to the Goldschmidt process (p. 380) to produce ferro-molybdenum. Ammonium molybdate, obtained by treating the trioxide with sufficient aqueous ammonia to dissolve it and then evaporating the solution, is the common laboratory source of molybdenum compounds. The salt has the complex composition $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, but a solution of the simple molybdate $(\text{NH}_4)_2\text{MoO}_4$ is formed by dissolving it in excess of aqueous ammonia.

Properties and Uses of Molybdenum. Molybdenum belongs to the small class of 'refractory' metals, with melting-points exceeding 2,500°:

Molybdenum	Osmium	Tantalum	Rhenium	Tungsten
2,620°	2,700°	2,996°	3,167°	3,370°

and is consequently used to form the 'spider' supporting the filaments of the even higher melting tungsten in incandescent electric lamps. The metal is usually seen as a grey powder, but this may be compacted into a coherent metal, closely resembling platinum in colour, by heating electrically under pressure in an atmosphere of hydrogen.

Molybdenum steels, containing up to 10 per cent of molybdenum, retain their hardness unimpaired up to about 500°, or low red heat;

they are often described as possessing 'red-hardness.' Such alloys are therefore a preferred material for '*high-speed*' tools, used in machining operations when the inevitable rise of temperature would destroy the 'temper' of ordinary steel, unless the operations were conducted at an uneconomically slow speed. It could hardly be denied that the introduction of such steels has made possible the modern mass-production in the engineering industries.

Compounds of Molybdenum. These are exceptionally numerous, since the element exists in no less than four valency states, III–VI inclusive, corresponding to the set of oxides Mo_2O_3 , MoO_2 , Mo_2O_5 , and MoO_3 , all of which except the last are wholly basic in function. A feebly basic function is shown even by the trioxide, which is dissolved by strong acids. When 5-normal nitric acid is gradually added to a solution of ammonium molybdate the sparingly soluble (hydrated) trioxide is first precipitated, but on addition of an excess of acid it passes again into solution, probably as the salt $\text{MoO}_2(\text{NO}_3)_2$. On addition of phosphate to the nitric acid solution the characteristic and well-known yellow precipitate appears.

EXTRACTION OF TUNGSTEN

TUNGSTEN, W

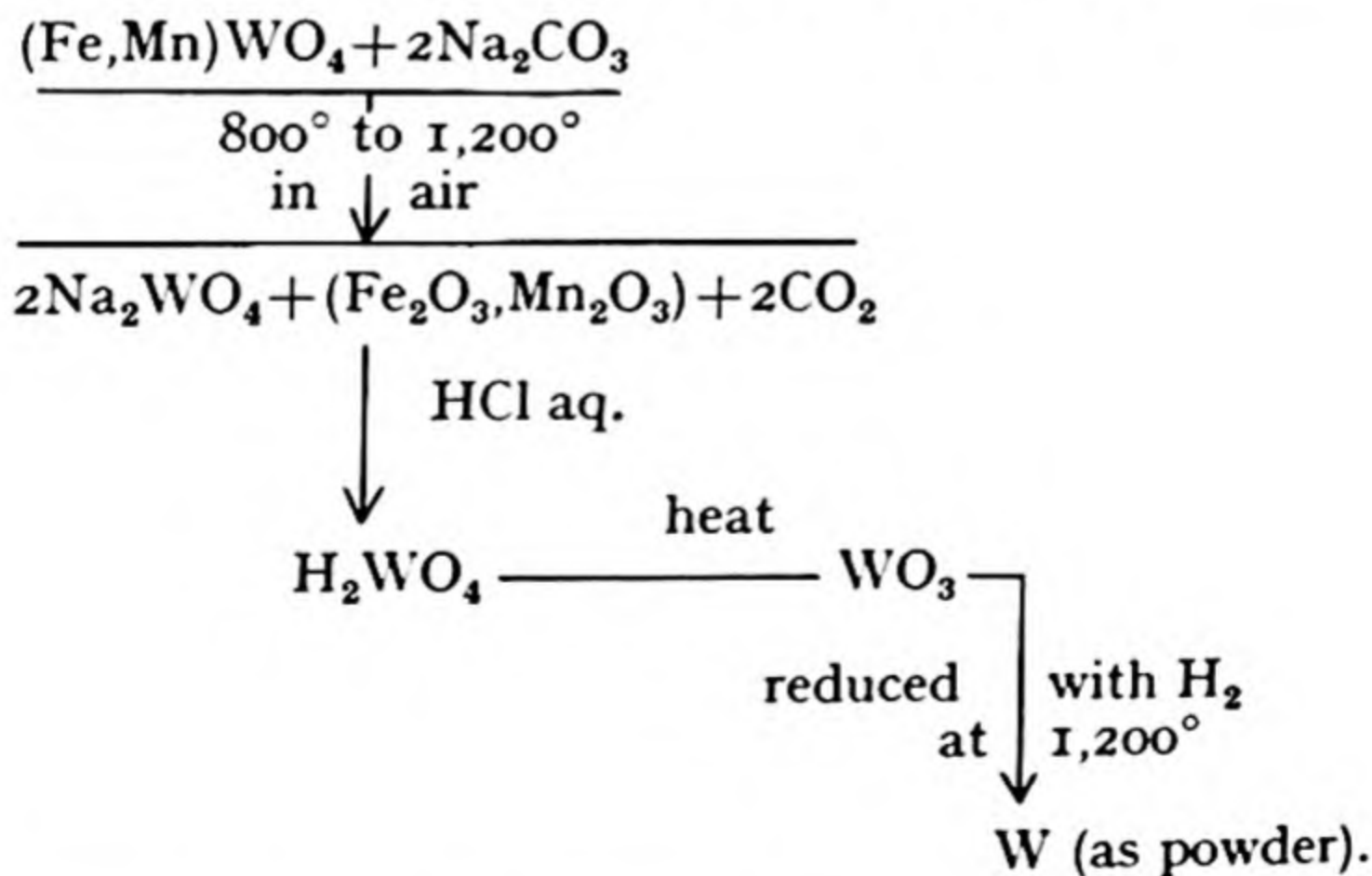
Group VIA. Atomic number: 74. Atomic weight: 183.86. Specific gravity: 19.3. Melting-point: 3,370°.

Historical. Both the names *tungsten* and *wolfram* (from which the symbol W is derived) were originally applied to principal ores of the metal; the former, which means 'heavy stone,' to *scheelite*, or calcium tungstate, CaWO_4 ; and the latter to the mineral now called *wolframite*, which is a mixture of ferrous and manganous tungstate $(\text{Fe, Mn})\text{WO}_4$. Wolframite often occurs in association with cassiterite, the chief ore of tin (p. 412), and there appears to have been an early belief that evil influences had despoiled the coveted tin by conversion to the then useless wolfram, 'as the wolf despoils the sheep.' A sixteenth-century metallurgical treatise refers to wolframite as 'lupa spuma,' wolf's spittle (cf. nickel, p. 601).

In 1781 SCHEELE characterized as calcium tungstate the mineral now termed in commemoration *scheelite*; the metal, however, was first isolated from wolframite in 1783 by the Spanish chemists, the brothers D'ELHUJAR. Tungsten is now the only element with a symbol not linguistically related to its name, but recent suggestions to revert to the name wolfram have not been generally accepted.

Extraction.

- (1) As pure metal required for electric incandescent lamp filaments (2-4 per cent of world production):



The metallic powder is converted into a coherent ductile form suitable for wire-drawing by a complicated process of sintering and hammering ('swaging') at high temperature.

- (2) Ferro-tungsten for the manufacture of tungsten alloy steels (taking about 95 per cent of world production) is obtained by the Goldschmidt process (p. 380).

Properties and Uses of Tungsten. The melting-point of tungsten ($3,370^{\circ}$) exceeds those of all other known elements except carbon (M.P. $3,500^{\circ}$). The appearance of the coherent metal together with that of the supporting molybdenum 'spider' may be inspected (with the aid of some magnification) within any clear-glass electric incandescent lamp bulb. Tungsten is one of the heaviest three metals—W, 19.3; Au, 19.3; Pt, 21.4 gm./c.c.—and also resembles platinum and gold in its inertness to many chemical reagents.

Tungsten alloy steels, used as early as 1855, and containing up to 20 per cent of tungsten, have, like molybdenum steels, the property of 'red-hardness', making them indispensable for all purposes when hardness must be maintained at high temperature, such as in high-speed tools and in parts of modern aircraft engines.

Compounds of Tungsten. Tungsten exists in the same set of valency states (III–VI inclusive) as molybdenum, and its numerous compounds closely resemble the corresponding compounds of that metal. In industry the carbide, of composition WC, has assumed great importance. As hard as diamond and alloyed with some nickel or cobalt to minimize its brittleness, the carbide is widely used for tipping drills and edging other tools operating on refractory materials.

ATOMIC NUMBERS AND WEIGHTS

SYMBOL	NAME	ATOMIC NUMBER	ATOMIC WEIGHT
H	Hydrogen	1	1.0080
He	Helium	2	4.003
Li	Lithium	3	6.940
Be	Beryllium	4	9.013
B	Boron	5	10.82
C	Carbon	6	12.011
N	Nitrogen	7	14.008
O	Oxygen	8	16.0000
F	Fluorine	9	19.00
Ne	Neon	10	20.183
Na	Sodium	11	22.991
Mg	Magnesium	12	24.32
Al	Aluminium	13	26.98
Si	Silicon	14	28.09
P	Phosphorus	15	30.975
S	Sulphur	16	32.066
Cl	Chlorine	17	35.457
A	Argon	18	39.944
K	Potassium	19	39.100
Ca	Calcium	20	40.08
Sc	Scandium	21	44.96
Ti	Titanium	22	47.90
V	Vanadium	23	50.95
Cr	Chromium	24	52.01
Mn	Manganese	25	54.94
Fe	Iron	26	55.85
Co	Cobalt	27	58.94
Ni	Nickel	28	58.71
Cu	Copper	29	63.54
Zn	Zinc	30	65.38
Ga	Gallium	31	69.72
Ge	Germanium	32	72.60
As	Arsenic	33	74.91
Se	Selenium	34	78.96
Br	Bromine	35	79.916
Kr	Krypton	36	83.80
Rb	Rubidium	37	85.48
Sr	Strontium	38	87.63
Y	Yttrium	39	88.92
Zr	Zirconium	40	91.22
Nb	Niobium	41	92.91
Mo	Molybdenum	42	95.95
Tc	Technetium	43	(99)
Ru	Ruthenium	44	101.1
Rh	Rhodium	45	102.91
Pd	Palladium	46	106.4

ATOMIC NUMBERS AND WEIGHTS—*continued*

SYMBOL	NAME	ATOMIC NUMBER	ATOMIC WEIGHT
Ag	Silver	47	107.880
Cd	Cadmium	48	112.41
In	Indium	49	114.82
Sn	Tin	50	118.70
Sb	Antimony	51	121.76
Te	Tellurium	52	127.61
I	Iodine	53	126.91
Xe	Xenon	54	131.30
Cs	Caesium	55	132.91
Ba	Barium	56	137.36
La	Lanthanum	57	138.92
Ce	Cerium	58	140.13
Pr	Praseodymium	59	140.92
Nd	Neodymium	60	144.27
Pm	Promethium	61	(145)
Sm	Samarium	62	150.35
Eu	Europium	63	152.0
Gd	Gadolinium	64	157.26
Tb	Terbium	65	158.93
Dy	Dysprosium	66	162.51
Ho	Holmium	67	164.94
Er	Erbium	68	167.27
Tm	Thulium	69	168.94
Yb	Ytterbium	70	173.04
Lu	Lutetium	71	174.99
Hf	Hafnium	72	178.50
Ta	Tantalum	73	180.95
W	Tungsten	74	183.86
Re	Rhenium	75	186.22
Os	Osmium	76	190.2
Ir	Iridium	77	192.2
Pt	Platinum	78	195.09
Au	Gold	79	197.0
Hg	Mercury	80	200.61
Tl	Thallium	81	204.39
Pb	Lead	82	207.21
Bi	Bismuth	83	209.00
Po	Polonium	84	210
At	Astatine	85	(210)
Rn	Radon	86	222
Fr	Francium	87	(223)
Ra	Radium	88	226.05
Ac	Actinium	89	227
Th	Thorium	90	232.05
Pa	Protoactinium	91	231
U	Uranium	92 *	238.07

* For the transuranic elements, see p. 100.

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